

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>A61K 7/00</b>	<b>A2</b>	<b>(11) International Publication Number:</b> <b>WO 00/61080</b> <b>(43) International Publication Date:</b> 19 October 2000 (19.10.00)
<b>(21) International Application Number:</b> PCT/GB00/01235 <b>(22) International Filing Date:</b> 31 March 2000 (31.03.00) <b>(30) Priority Data:</b> 9908212.5 12 April 1999 (12.04.99) GB <b>(71) Applicant (for AE AU BB CA CY DM GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZA ZW only):</b> UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). <b>(71) Applicant (for all designated States except AE AU BB CA CY DM GB GD GH GM IE IL IN KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZA ZW):</b> UNILEVER NV [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). <b>(71) Applicant (for IN only):</b> HINDUSTAN LEVER LIMITED [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Mumbai 400 020 (IN). <b>(72) Inventors:</b> FRANKLIN, Kevin, Ronald; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). HOPKINSON, Andrew; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB).		<b>(74) Agent:</b> BAKER, Colin, J.; Eric Potter Clarkson, Park View House, 58 The Ropewalk, Nottingham NG1 5DD (GB). <b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> COSMETIC COMPOSITIONS <b>(57) Abstract</b> <p>A cosmetic composition contains a water-immiscible carrier liquid and a structurant therefor which is effective to gel the composition upon cooling from a temperature at which the structurant is a mobile solution in the carrier liquid. The carrier liquid may serve as a continuous phase in which a solid or liquid disperse phase is suspended. The structurant is a fully or partially esterified saccharide which contains no more than eight monosaccharide residues and has an enthalpy of gelation in the carrier liquid with a magnitude of at least 45 kJ/mole. This minimum enthalpy of gelation facilitates processing at conveniently accessible temperatures and promotes stability.</p>		

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

COSMETIC COMPOSITIONSFIELD OF THE INVENTION

5

The present invention relates to cosmetic compositions for application to human skin. Significant forms of the invention are concerned with antiperspirant compositions for application to human skin, especially the axilla. However, the invention can also be applied to other forms of cosmetic composition.

BACKGROUND OF THE INVENTION AND SUMMARY OF PRIOR ART

15 A wide variety of cosmetic compositions for application to human skin make use of a thickened or structured liquid carrier to deliver colour or some other active material to the surface of the skin. A significant example of such cosmetic compositions are antiperspirant compositions which are widely used in order to enable their users to avoid or minimise wet patches on their skin, especially in axillary regions.

25 Cosmetic compositions have been made in a variety of product forms. One of these is a so-called "stick" which is usually a bar of an apparently firm solid material

held within a dispensing container and which retains its structural integrity and shape whilst being applied.

When a portion of the stick is drawn across the skin surface a film of the stick composition is transferred to the skin surface. Although the stick has the appearance of a solid article capable of retaining its own shape for a period of time, the material usually has a structured liquid phase so that a film of the composition is readily transferred from the stick to another surface upon contact. Examples of cosmetic compositions which are, or can be, marketed in a stick form are lipsticks, lip salves and eyebrow pencils. The stick form has been used in particular for deodorant and antiperspirant compositions where the composition includes a deodorant active material or an antiperspirant active material respectively.

Another possibility is that a stick is a softer solid composition accommodated in a dispensing container which in use extrudes the composition through one or more apertures.

Antiperspirant sticks and other cosmetic compositions can be divided into three categories.

Suspension sticks contain a particulate material, notably a particulate antiperspirant active material, suspended

in a structured carrier liquid phase. Emulsion sticks normally have a hydrophilic phase forming an emulsion with a second, more hydrophobic, liquid phase. One of the phases contains an active material. Solution sticks  
5 typically have the active material dissolved in a structured liquid phase; this phase may be organic solvent or may be a mixture of water and a water-miscible organic solvent. This classification into suspension, emulsion and solution types can be applied to both firm  
10 and soft solid compositions.

Besides firm and soft sticks, a number of cosmetic compositions have taken the form of liquids which are formulated to be somewhat viscous and hence pour and flow  
15 more slowly than water. One example is antiperspirant compositions in liquid form, such as applied using a roll-on applicator.

There is substantial literature on the structuring  
20 or thickening of cosmetic compositions which is frequently accomplished using some form of thickening agent as part of the composition.

Some compositions have a substantial viscosity,  
25 which may even make them capable of retaining their own shape for a time, because of transient interactions

between molecules of a thickening agent in the liquid.

This is characteristic of compositions which are thickened with polymers. Thickening can be attributed to  
5 interactions between polymer molecules.

It is characteristic of such thickened compositions that their viscosity can be achieved or recovered on standing at room temperature. If subjected to shear  
10 their viscosity reduces (hence they are described as shear thinning) but the viscosity recovers towards its original value if the composition is subsequently allowed to stand at room temperature.

15 Compositions which have two phases, i.e. compositions which are an emulsion or a suspension may also have substantial viscosity, even to the extent of being able to sustain their own shape.

20 Here too it is characteristic of the composition that - provided the composition is stable - its viscosity will recover spontaneously if it is reduced by subjecting the composition to shear.

25 Compositions have also been given structure and an enhanced viscosity or rigidity by the incorporation of a

structurant (also referred to as a gellant or gelling agent) which causes the liquid to gel upon cooling from an elevated temperature.

5        Gel formation takes place as an exothermic event within a temperature range referred to as the gel point or gel temperature. Upon reheating, melting of the gel takes place as an endothermic event within a temperature range. When the gel melts, the structurant goes into  
10        solution in the liquid. Such gels can be disrupted by shearing and do not recover their viscosity for a long time, if at all unless remelted, although a small partial recovery may be observed.

15        One material which is well known to form gels is 12-hydroxystearic acid which is discussed in Terech et al "Organogels and Aerogels of Racemic and Chiral 12-hydroxy octadecanoic Acid", Langmuir Vol 10, 3406-3418, 1994. The material is commercially available from Ajinomoto and  
20        from Caschem.

US-A-5750096 and US-A-5489276 are two of several documents which teaches that gelation can be brought about using esters or amides of 12-hydroxystearic acid.

25

In these documents, especially the latter, there is

a proposal to enhance the efficacy of 12-hydroxystearic acid or other gellant by including a "nucleating agent". A range of possibilities for the nucleating agent are suggested, including esterified sucrose. The only  
5 function attributed to that material is to modify or promote the gelating action of another material.

Gelation with a waxy material, especially stearyl alcohol, has been mentioned in a great many documents.  
10 WO-A-98/43605 is a recent example.

N-acyl amino acid amides and esters are also known to structure liquids. We have established that they do so by forming fibrous networks. They are described in US  
15 patent 3969087. N-Lauroyl-L-glutamic acid di-n-butylamide is commercially available from Ajinomoto under their designation GP-1.

Further materials which have been disclosed as  
20 gelling agents are the amide derivatives of di and tribasic carboxylic acids set forth in WO 98/27954 notably alkyl N,N'dialkyl succinamides.

Yet another example of material which can be used to  
25 bring about gelation of a hydrophobic carrier liquid is lanosterol, as described in WO 97/11673 where it is used



in the preparation of soft, opaque gels as antiperspirant compositions WO 98/34588 also describes the use of lanosterol as a gellant for oil-based cosmetic compositions.

5

#### SUMMARY OF THE INVENTION

We have recognised that when a gel is formed, the solution of the structurant in a liquid may supercool before gelling commences, and in consequence the gel-melting temperature may be higher than the gel-formation temperature. If gel-formation takes place in a quiescent solution of the structurant the extent of supercooling may be substantial. We have observed that it varies from one structurant to another.

However, if the structurant is being used to prepare a product where a constituent such as a disperse phase is mixed into the hot liquid before gel formation, we have found that it is likely to be necessary to carry out this mixing operation at a temperature at which the structurant is fully soluble in the liquid. If an attempt is made to mix the composition at a temperature at which there is some supercooling, it is likely that the mixing will induce gelation to commence.

It is a consequence of this that when preparing structured liquid compositions containing a structurant to gel the liquid, all constituents of the composition must be subjected to a temperature high enough to  
5 dissolve the structuring agent.

We have now found that advantageous properties and processing can be provided by utilising as gelling agent an esterified saccharide which has an enthalpy of gelation  
10 of at least 45 kiloJoule per mole.

According to a first aspect of this invention there is provided a cosmetic composition comprising a water-immiscible carrier liquid and a structurant therefor  
15 which is effective to gel the composition upon cooling from a temperature at which the structurant is a mobile solution in the carrier liquid, characterised in that the structurant is a wholly or partially esterified saccharide which contains no more than eight  
20 monosaccharide residues and which has an enthalpy of gelation in the carrier liquid of at least 45 kJ/mole, preferably at least 48 kJ/mole or 50 kJ/mole.

The enthalpy of gelation can be determined by  
25 differential scanning calorimetry (DSC).

We have found that if the enthalpy of gelation is high (45 kJ per mole or more) compositions can be prepared with two advantages. One is that a composition can be prepared using moderate processing temperatures (which we have found to be important). The other is that the resulting gel is stable. By contrast, if the enthalpy of gelation is low, one or both of two disadvantages are observed. Rather high processing temperatures may be needed and/or a gel may be formed but then undergo unwanted progressive transformation during storage, such as crystals appearing and growing, softening of the composition or leakage of liquid from it.

Although the enthalpy of gelation is a property of the structurant and carrier liquid jointly, we have found that it is predominantly a property of the structurant. Consequently, the measurement of enthalpy of gelation in one or several representative liquids is valuable as technique (which can be carried out with a small sample and a standard instrument) to assess the suitability of a potential structurant. It may be desirable to take a measurement in any one of several representative liquids, since some structurants do not gel all hydrophobic carrier liquids. However, we have found that an 80:20 wt% mixture of decamethyl cyclopentasiloxane and

isostearyl alcohol is generally suitable when assessing the suitability of a potential esterified saccharide structurant.

5       Therefore in a second aspect this invention provides a cosmetic composition comprising a water-immiscible carrier liquid and a structurant therefor which is effective to gel the composition upon cooling from a temperature at which the structurant is a mobile solution  
10 in the carrier liquid, characterised in that the structurant is a wholly or partially esterified saccharide which contains no more than eight monosaccharide residues and which structurant is able to gel an 80:20 wt% mixture of decamethyl cyclopentasiloxane  
15 and isostearyl alcohol with an enthalpy of gelation of at least 45 kJ/mole, preferably at least 48 or 50 kJ/mole.

The esterified saccharide structurant will generally be such as to exist in the form of a network of fibres or  
20 strands within the water-immiscible carrier liquid.

Preferably the structurant contains at least two but no more than five monosaccharide residues and is esterified at a majority of the esterified hydroxy  
25 groups.

Preferably the average number of carbon atoms in the esterifying acyl groups is at least 6, more preferably is from 6 to 8 up to 18 carbon atoms.

5        A composition of this invention may be a structured solution with active ingredient or colourant dissolved in the carrier liquid, or it may be a composition with a dispersed second phase, either a suspension with a solid active ingredient dispersed in the carrier liquid or an  
10        emulsion with a second liquid phase dispersed in the carrier liquid. The second liquid phase may then be a solution of an antiperspirant active in a hydrophilic solvent.

15        A composition according to this invention may take the form of a firm gel with apparent rigidity, or a soft solid which is able to retain its own shape for a time (for example if it is taken out of a mould without being subjected to shear) but which is easily deformed by hand  
20        pressure. Preferred within this invention are compositions which have sufficient rigidity that they can be regarded as firm solids. The hardness of such compositions can be measured with a penetrometer, in a manner which will be described in greater detail below.

25

Certain preferred forms of this invention are

concerned with compositions which are translucent or transparent. As is already known, translucent or transparent compositions can be obtained if it is possible to match the refractive indices of the different  
5 constituent phases present in the composition.

We have found that compositions within this invention which are a novel transparent or translucent emulsion can be obtained by formulating the composition  
10 to meet two criteria. Firstly the disperse phase and the continuous phase (consisting of the water-immiscible carrier liquid and the structurant contained within that liquid) should be formulated so that their refractive indices match. The refractive index of the continuous  
15 phase will be close to the refractive index of the water-immiscible carrier liquid in it. In order to achieve good light transmission through a composition, the refractive index of the water-immiscible continuous phase and the refractive index of the disperse phase should  
20 match within 0.003 units preferably 0.002 units.

Secondly, the matched refractive indices of these two phases should lie in a range which is an approximate match to the refractive index of the structurant. The  
25 closeness of match required will depend on the structurant which is used. The refractive index of a

structurant can be determined by making trial compositions as explained in more detail below. Such investigation will also show how closely the refractive index of the liquid must be matched to the structurant.

5

A composition of this invention will generally be marketed in a container by means of which it can be applied at time of use. This container may be of conventional type.

10

Another aspect of the invention therefore provides a cosmetic composition comprising a dispensing container having at least one aperture for delivery of the contents of the container, means for urging the contents of the container to the said aperture or apertures, and a composition of either of the previous aspects of the invention in the container. Preferred is that a composition of this invention is sufficiently rigid to be accommodated as a stick product in a dispensing container having an open end at which an end portion of the stick of composition is exposed for use.

15  
20

The compositions of this invention can be produced by processes in which the composition is produced as a mobile liquid at an elevated temperature and allowed to cool to permit gel-formation.

25

Thus, according to a further aspect of the present invention there is provided a process for the production of an antiperspirant composition comprising, not necessarily in any order, the steps of

- 5 • incorporating an esterified saccharide structurant into a water-immiscible liquid carrier
- optionally mixing the liquid carrier with a disperse solid or liquid phase,
- heating the liquid carrier or a mixture containing it  
10 to an elevated temperature at which the structurant is soluble in the water-immiscible liquid carrier,  
suitably followed by
- introducing the mixture into a mould which  
15 preferably is a dispensing container, and then
- cooling or permitting the mixture to cool to a temperature at which it is thickened or solidified.

In this invention it is possible and indeed  
20 preferred that the step of mixing with a disperse phase, and any subsequent steps, are carried out at a temperature not exceeding 90°C and possibly not exceeding 85°C.

It may be possible to keep below these temperatures  
25 throughout the process.



According to a yet further aspect of the present invention, there is provided a method for preventing or reducing perspiration on human skin comprising topically applying to the skin a composition as set forth earlier  
5 comprising an antiperspirant active, a water-immiscible liquid carrier and an esterified saccharide structurant therefor.

#### DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS

10

Measurement of enthalpy of gelation can be carried out using a small sample and standard DSC techniques.

Measurement should be carried out at a slow cooling  
15 rate and to promote consistency in measurement, it should, if possible, be carried out with the concentration in a standardised range or approximating to a standard value.

20 We have preferred to carry out measurement at a concentration of structurant in the liquid which is not over 8% by weight, preferably from 3%, better 6%, up to 8% by weight. Results at such concentrations are generally a close approximation to results at a  
25 standardised concentration of 7.5% by weight.

For any structurant which cannot dissolve at such a concentration, an alternative standardised concentration would be 3% by weight.

5        A gel may first be made by heating and cooling, and a sample of gel sealed in a calorimeter capsule. Alternatively the appropriate weights of liquid and structurant could be sealed in a calorimeter capsule, heated and allowed to cool to a gel in the capsule.

10

In a preferred procedure a gel is prepared containing from 7 to 7.5% by weight of structuring agent. Approximately 20mg of the gel (for example between 18 and 22 mg) is weighed into a calorimeter capsule and sealed.

15       It is then heated at 10K/minute to a temperature at which the structuring agent is known to be fully soluble in the liquid, held for one minute at this temperature and then a DSC scan is taken while cooling at 2K/minute.

20       The scan is repeated with a capsule containing approximately 20mg of decamethyl cyclopentadisiloxane and in accordance with normal DSC technique, data collected with the liquid alone (multiplied by a scaling factor if necessary) is subtracted from the data collected with the  
25       gel, so that the gel-formation exotherm appears as a departure from a flat baseline. The enthalpy is the area

between the peak and the baseline.

We have found it appropriate to carry out measurements, both on the gel and on the liquid alone,  
5 over a broad range of temperatures, such as from -50°C to +150°C for the sake of accuracy in subtracting one measurement from the other.

For calculation it is assumed that the exotherm  
10 (heat given out during gel formation) comes from the whole quantity of structuring agent present.

#### Structurant

15 A number of organic compounds are known to possess the ability to gel hydrophobic organic liquids such as water-immiscible hydrocarbon and/or silicone oils by formation of a network of fibres or strands which extends throughout the liquid, thereby gelling the liquid. Such  
20 materials are generally non-polymeric, being monomers or dimers with molecular weight below 10,000 rather than polymers with more than 8 repeat units or with molecular weight above 10,000.

Materials with this property have been reviewed by  
25 Terech and Weiss in "Low Molecular Mass Gelators of

Organic Liquids and the Properties of their Gels" Chem.  
Rev 97, 3133-3159 [1997] and by Terech in Chapter 8,  
"Low-molecular weight Organogelators" of the book  
"Specialist surfactants" edited by I D Robb, Blackie  
5 Academic Professional, 1997.

It is characteristic of such structurants that

- they are able to gel the organic liquid in the  
absence of any disperse phase
- 10 • the structured liquids are obtainable by cooling  
from an elevated temperature at which the  
structurant is in solution in the liquid - this  
solution being mobile and pourable
- the structured liquid becomes more mobile if  
15 subjected to shear or stress
- the structure does not spontaneously recover within  
24 hours if the sheared liquid is left to stand at  
room temperature even though a small partial  
recovery may be observed
- 20 • the structure can be recovered by reheating to a  
temperature at which the structurant is in solution  
in the liquid, and allowing it to cool back to room  
temperature.

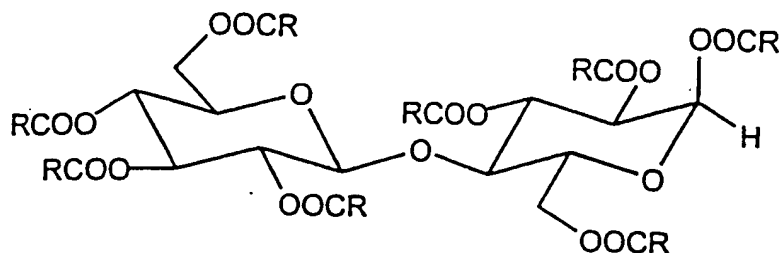
25 It appears that such structurants operate by  
interactions which are permanent unless disrupted by

shear or heating. Such structurants operate by forming a network of strands or fibres extending throughout the gelled liquid. In some cases these fibres can be observed by electron microscopy, although in other cases the observation of the fibres which are believed to be present is prevented by practical difficulties in preparing a suitable specimen. When observed, the fibres in a gel are generally thin (diameter less than  $0.5\mu$ , often less than  $0.2\mu$ ) and appear to have numerous branches or interconnections.

From our observations made using differential scanning calorimetry we believe that fibrous networks consist of crystalline material. The crystalline fibres may or may not be the same polymorph as macroscopic crystals obtained by conventional crystallization from a solvent.

A novel structurant which is the subject of a co-pending application and which may be used in this invention is an ester of cellobiose and a fatty acid, preferably of 6 to 13 carbon atoms especially 8 to 11 carbon atoms. Preferably the cellobiose is fully esterified, or nearly so, and is in the  $\alpha$ -anomeric form.

The structure of such a compound in its  $\alpha$ -anomeric form is:



- 5 where R is an alkyl or alkenyl chain of 5 to 12 carbon atoms so that the acyl group contains 6 to 13 carbon atoms. Particularly preferred acyl groups incorporate a linear alkyl chain of 7 to 9 or 10 carbon atoms and are thus octanoyl, nonanoyl, decanoyl or undecanoyl.

10

- The acyl groups may have a mixture of chain lengths but it is preferred that they are similar in size and structure. Thus it is preferred that all of the acyl groups are aliphatic and at least 90% of the acyl groups
- 15 have a chain length within a range such that the shorter and longer chain lengths in the range differ by no more than two carbon atoms, i.e. length in a range from  $m - 1$  to  $m + 1$  carbon atoms where the mean acyl chain length  $m$  has a value in a range from 7 to 10 or 11. Commercially
- 20 available feedstocks for these acyl groups are likely to include a small percentage of acyl groups which differ

from the majority and may have a branched rather than linear chain. Thus it is likely that more than 90% but less than 100% of the acyl groups will meet the desired criterion of chain lengths in a range from  $m - 1$  to  $m + 1$  carbon atoms.

Linear aliphatic acyl groups may be obtained from natural sources, in which case the number of carbon atoms in the acyl group is likely to be an even number or may be derived synthetically from petroleum as the raw material in which case both odd and even numbered chain lengths are available.

Synthetic methods for the esterification of saccharides are well known. The esterification of cellobiose has been reported by Takada et al in *Liquid Crystals*, (1995) Volume 19, pages 441-448.. This article gives a procedure for the production of the alpha anomers of cellobiose octa-alkanoates by esterification of  $\beta$ -cellobiose using an alkanoic acid together with trifluoroacetic anhydride.

For this invention the structurant is a material from this category discussed above but selected so that it also satisfies the criterion of an enthalpy of gelation exceeding 45 kiloJoule per mole.

Carrier liquid

The water-immiscible carrier liquid in the continuous phase comprises one or a mixture of materials which are relatively hydrophobic so as to be immiscible in water. Some hydrophilic liquid may be included in the carrier, provided the overall carrier liquid mixture is immiscible with water. It will generally be desired that this carrier is liquid (in the absence of structurant) at temperatures of 15°C and above. It may have some volatility but its vapour pressure will generally be less than 4 kPa (30mmHg) at 25°C so that the material can be referred to as an oil or mixture of oils. More specifically, it is desirable that at least 80% by weight of the hydrophobic carrier liquid should consist of materials with a vapour pressure not over this value of 4 kPa at 25°C.

It is preferred that the hydrophobic carrier material includes a volatile liquid silicone, i.e. liquid polyorganosiloxane. To class as "volatile" such material should have a measurable vapour pressure at 20 or 25°C. Typically the vapour pressure of a volatile silicone lies in a range from 1 or 10 Pa up to 2 kPa at 25°C.

It is desirable to include volatile silicone because



it gives a "drier" feel to the applied film after the composition is applied to skin.

Volatile polyorganosiloxanes can be linear or cyclic or mixtures thereof. Preferred cyclic siloxanes include polydimethylsiloxanes and particularly those containing from 3 to 9 silicon atoms and preferably not more than 7 silicon atoms and most preferably from 4 to 6 silicon atoms, otherwise often referred to as cyclomethicones.

Preferred linear siloxanes include polydimethylsiloxanes containing from 3 to 9 silicon atoms. The volatile siloxanes normally by themselves exhibit viscosities of below  $10^{-5}$  m<sup>2</sup>/sec (10 centistokes), and particularly above  $10^{-7}$  m<sup>2</sup>/sec (0.1 centistokes), the linear siloxanes normally exhibiting a viscosity of below  $5 \times 10^{-6}$  m<sup>2</sup>/sec (5 centistokes). The volatile silicones can also comprise branched linear or cyclic siloxanes such as the aforementioned linear or cyclic siloxanes substituted by one or more pendant -O-Si(CH<sub>3</sub>)<sub>3</sub> groups. Examples of commercially available silicone oils include oils having grade designations 344, 345, 244, 245 and 246 from Dow Corning Corporation; Silicone 7207 and Silicone 7158 from Union Carbide Corporation; and SF1202 from General Electric.

25

The hydrophobic carrier employed in compositions

herein can alternatively or additionally comprise non-volatile silicone oils, which include polyalkyl siloxanes, polyalkylaryl siloxanes and polyethersiloxane copolymers. These can suitably be selected from dimethicone and  
5 dimethicone copolyols. Commercially available non-volatile silicone oils include Dow Corning 556 and Dow Corning 200 series.

The water-immiscible liquid carrier may contain from  
10 0 to 100% by weight of one or more liquid silicones. Preferably, there is sufficient liquid silicone to provide at least 10%, better at least 15%, by weight of the whole composition. If silicone oil is used, volatile silicone preferably lies in a range from 20% possibly from 30 or  
15 40% up to 100% of the weight of the water-immiscible carrier liquid. In many instances, when a non-volatile silicone oil is present, its weight ratio to volatile silicone oil is chosen in the range of from 1:3 to 1:40.

20 Silicon-free hydrophobic liquids can be used instead of, or more preferably in addition to liquid silicones. Silicon-free hydrophobic organic liquids which can be incorporated include liquid aliphatic hydrocarbons such as mineral oils or hydrogenated polyisobutene, often selected  
25 to exhibit a low viscosity. Further examples of liquid hydrocarbons are polydecene and paraffins and isoparaffins

of at least 10 carbon atoms.

Other hydrophobic carriers are liquid aliphatic or aromatic esters.

5

Suitable aliphatic esters contain at least one long chain alkyl group, such as esters derived from C<sub>1</sub> to C<sub>20</sub> alkanols esterified with a C<sub>6</sub> to C<sub>22</sub> alkanolic acid or C<sub>6</sub> to C<sub>10</sub> alkanedioic acid. The alkanol and acid moieties or  
10 mixtures thereof are preferably selected such that they each have a melting point of below 20°C. These esters include isopropyl myristate, lauryl myristate, isopropyl palmitate, diisopropyl sebacate and diisopropyl adipate.

15

Suitable liquid aromatic esters, preferably having a melting point of below 20°C, include fatty alkyl benzoates. Examples of such esters include suitable C<sub>6</sub> to C<sub>18</sub> alkyl benzoates or mixtures thereof.

20

Further instances of suitable hydrophobic carriers comprise liquid aliphatic ethers derived from at least one fatty alcohol, such as myristyl ether derivatives e.g. PPG-3 myristyl ether or lower alkyl ethers of  
25 polyglycols such as PPG-14 butyl ether.

Aliphatic alcohols which are solid at 20°C, such as stearyl alcohol are preferably absent or present in low concentration such as less than 5% by weight of the whole composition since these lead to visible white deposits  
5 when a composition is used.

However, aliphatic alcohols which are liquid at 20°C may be employed. These include branched chain alcohols of at least 10 carbon atoms such as isostearyl alcohol and  
10 octyl dodecanol.

Very polar materials are preferably excluded or present in only small quantity in the water-immiscible carrier liquid. Preferably therefore, this liquid or  
15 mixture of liquids contains not more than 10% of its own weight, better not more than 5%, of any constituent which is a water-miscible compound.

Silicon-free liquids can constitute from 0-100% of  
20 the water-immiscible liquid carrier, but it is preferred that silicone oil is present and that the amount of silicon-free constituents preferably constitutes up to 50 or 60% and in many instances from 10 or 15% up to 50 or 60% by weight of the carrier liquid.

25

If any oxygen-containing silicon-free organic

liquids are included in the hydrophobic carrier liquid, the amount of them is likely to be not over 70% by weight of the carrier liquid. Smaller amounts, ranging up to 20, 30 or 35% by weight are likely.

5

The carrier liquid must be compatible with the structurant. If the structurant is too soluble or conversely is very insoluble in the carrier liquid it may fail to form a gel and the carrier liquid should be

10 modified to alter its polarity.

Liquid Disperse Phase

If the composition is an emulsion in which the esterified saccharide acts as a structurant in the continuous phase, the emulsion will contain a more polar disperse phase. The disperse phase may be a solution of an active ingredient.

The hydrophilic disperse phase in an emulsion normally comprises water as solvent and can comprise one or more water soluble or water miscible liquids in addition to or replacement for water. The proportion of water in an emulsion according to the present invention is often selected in the range of up to 60%, and particularly from 10% up to 40% or 50% of the whole formulation.

One class of water soluble or water-miscible liquids comprises short chain monohydric alcohols, e.g. C<sub>1</sub> to C<sub>4</sub> and especially ethanol or isopropanol, which can impart a deodorising capability to the formulation. A further class of hydrophilic liquids comprises diols or polyols preferably having a melting point of below 40°C, or which are water miscible. Examples of water-soluble or water-miscible liquids with at least one free hydroxy group include ethylene glycol, 1,2-propylene glycol, 1,3-

butylene glycol, hexylene glycol, diethylene glycol, dipropylene glycol, 2-ethoxyethanol, diethylene glycol monomethylether, triethyleneglycol monomethylether and sorbitol. Especially preferred are propylene glycol and  
5 glycerol.

In an emulsion the disperse phase is likely to constitute from 5 to 80 or 85% of the weight of the composition preferably from 5 to 50 or 65% more  
10 preferably from 25 or 35% up to 50 or 65%, while the continuous phase with the structurant therein provides the balance from 15 or 35% up to 95% of the weight of the composition. Compositions with a high proportion of disperse phase i.e. from 65 to 85% disperse phase may be  
15 advantageous because the large proportion of disperse phase can make a contribution to hardness.

An emulsion composition will generally include one or more emulsifying surfactants which may be anionic,  
20 cationic, zwitterionic and/or nonionic surfactants. The proportion of emulsifier in the composition is often selected in the range up to 10% by weight and in many instances from 0.1 or 0.25 up to 5% by weight of the composition. Most preferred is an amount from 0.1 or  
25 0.25 up to 3% by weight. Nonionic emulsifiers are frequently classified by HLB value. It is desirable to

use an emulsifier or a mixture of emulsifiers with an overall HLB value in a range from 2 to 10 preferably from 3 to 8.

5        It may be convenient to use a combination of two or more emulsifiers which have different HLB values above and below the desired value. By employing the two emulsifiers together in appropriate ratio, it is readily feasible to attain a weighted average HLB value that  
10 promotes the formation of an emulsion.

Many suitable emulsifiers of high HLB are nonionic ester or ether emulsifiers comprising a polyoxyalkylene moiety, especially a polyoxyethylene moiety, often  
15 containing from about 2 to 80, and especially 5 to 60 oxyethylene units, and/or contain a polyhydroxy compound such as glycerol or sorbitol or other alditol as hydrophilic moiety. The hydrophilic moiety can contain polyoxypropylene. The emulsifiers additionally contain a  
20 hydrophobic alkyl, alkenyl or aralkyl moiety, normally containing from about 8 to 50 carbons and particularly from 10 to 30 carbons. The hydrophobic moiety can be either linear or branched and is often saturated, though it can be unsaturated, and is optionally fluorinated.  
25 The hydrophobic moiety can comprise a mixture of chain lengths, for example those deriving from tallow, lard,



palm oil, sunflower seed oil or soya bean oil. Such nonionic surfactants can also be derived from a polyhydroxy compound such as glycerol or sorbitol or other alditols. Examples of emulsifiers include  
5 cetareth-10 to -25, ceteth-10-25, steareth-10-25 (i.e. C16 to C18 alcohols ethoxylated with 10 to 25 ethylene oxide residues) and PEG-15-25 stearate or distearate. Other suitable examples include C<sub>10</sub>-C<sub>20</sub> fatty acid mono, di or tri-glycerides. Further examples include C<sub>18</sub>-C<sub>22</sub>  
10 fatty alcohol ethers of polyethylene oxides (8 to 12 EO).

Examples of emulsifiers, which typically have a low HLB value, often a value from 2 to 6 are fatty acid mono  
15 or possibly diesters of polyhydric alcohols such as glycerol, sorbitol, erythritol or trimethylolpropane. The fatty acyl moiety is often from C<sub>14</sub> to C<sub>22</sub> and is saturated in many instances, including cetyl, stearyl, arachidyl and behenyl. Examples include monoglycerides  
20 of palmitic or stearic acid, sorbitol mono or diesters of myristic, palmitic or stearic acid, and trimethylolpropane monoesters of stearic acid.

A particularly desirable class of emulsifiers  
25 comprises dimethicone copolymers, namely polyoxyalkylene modified dimethylpolysiloxanes. The polyoxyalkylene

group is often a polyoxyethylene (POE) or polyoxypropylene (POP) or a copolymer of POE and POP. The copolymers often terminate in C<sub>1</sub> to C<sub>12</sub> alkyl groups.

- 5        Suitable emulsifiers and co-emulsifiers are widely available under many trade names and designations including Abil™, Arlacel™, Brij™, Cremophor™, Dehydrol™, Dehymuls™, Emerest™, Lameform™, Pluronic™, Prisorine™, Quest PGPR™, Span™, Tween™, SF1228, DC3225C and Q2-5200.
- 10

#### Antiperspirant Actives

- Antiperspirant actives, are preferably incorporated in an amount of from 0.5-60%, particularly from 5 to 30% or 40% and especially from 5 or 10% to 30 or 35% of the weight of the whole composition.
- 15

- Antiperspirant actives for use herein are often selected from astringent active salts, including in particular aluminium, zirconium and mixed aluminium/zirconium salts, including both inorganic salts, salts with organic anions and complexes. Preferred astringent salts include aluminium, zirconium and aluminium/zirconium halides and halohydrate salts, such as chlorohydrates.
- 20
- 25

Aluminium halohydrates are usually defined by the general formula  $Al_2(OH)_xQ_y \cdot wH_2O$  in which Q represents chlorine, bromine or iodine, x is variable from 2 to 5 and  $x + y = 6$  while  $wH_2O$  represents a variable amount of hydration. Especially effective aluminium halohydrate salts, known as activated aluminium chlorohydrates, are described in EP-A-6739 (Unilever NV et al), the contents of which specification is incorporated herein by reference. Some activated salts do not retain their enhanced activity in the presence of water but are useful in substantially anhydrous formulations, i.e. formulations which do not contain a distinct aqueous phase.

Zirconium actives can usually be represented by the empirical general formula:  $ZrO(OH)_{2n-nz}B_z \cdot wH_2O$  in which z is a variable in the range of from 0.9 to 2.0 so that the value  $2n-nz$  is zero or positive, n is the valency of B, and B is selected from the group consisting of chloride, other halide, sulphamate, sulphate and mixtures thereof. Possible hydration to a variable extent is represented by  $wH_2O$ . Preferable is that B represents chloride and the variable z lies in the range from 1.5 to 1.87. In practice, such zirconium salts are usually not employed by themselves, but as a component of a combined aluminium and zirconium-based antiperspirant.

The above aluminium and zirconium salts may have coordinated and/or bound water in various quantities and/or may be present as polymeric species, mixtures or complexes. In particular, zirconium hydroxy salts often  
5 represent a range of salts having various amounts of the hydroxy group. Zirconium aluminium chlorohydrate may be particularly preferred.

Antiperspirant complexes based on the above-  
10 mentioned astringent aluminium and/or zirconium salts can be employed. The complex often employs a compound with a carboxylate group, and advantageously this is an amino acid. Examples of suitable amino acids include dl-tryptophan, dl- $\beta$ -phenylalanine, dl-valine, dl-methionine  
15 and  $\beta$ -alanine, and preferably glycine which has the formula  $\text{CH}_2(\text{NH}_2)\text{COOH}$ .

It is highly desirable to employ complexes of a combination of aluminium halohydrates and zirconium  
20 chlorohydrates together with amino acids such as glycine, which are disclosed in US-A-3792068 (Luedders et al). Certain of those Al/Zr complexes are commonly called ZAG in the literature. ZAG actives generally contain aluminium, zirconium and chloride with an Al/Zr ratio in  
25 a range from 2 to 10, especially 2 to 6, an Al/Cl ratio from 2.1 to 0.9 and a variable amount of glycine.

**SUBSTITUTE SHEET (RULE 26)**

Actives of this preferred type are available from Westwood, from Summit and from Reheis.

Other actives which may be utilised include  
5 astringent titanium salts, for example those described in GB 2299506A.

The proportion of solid antiperspirant salt in a composition normally includes the weight of any water of  
10 hydration and any complexing agent that may also be present in the solid active. However, when active salt is in solution, it's weight excludes any water present.

If the composition is in the form of an emulsion the  
15 antiperspirant active will be dissolved in the disperse phase. In this case, the antiperspirant active will often provide from 3 to 60% by weight of the aqueous disperse phase, particularly from 10% or 20% up to 55% or 60% of that phase.

20

Alternatively, the composition may take the form of a suspension in which antiperspirant active in particulate form is suspended in the water-immiscible liquid carrier. Such a composition will probably not  
25 have any separate aqueous phase present and may conveniently be referred to as "substantially anhydrous"

although it should be understood that some water may be present bound to the antiperspirant active or as a small amount of solute within the water-immiscible liquid phase. In such compositions, the particle size of the antiperspirant salts often falls within the range of 0.1 to 200  $\mu\text{m}$  with a mean particle size often from 3 to 20  $\mu\text{m}$ .

Both larger and smaller mean particle sizes can also be contemplated such as from 20 to 50  $\mu\text{m}$  or 0.1 to 1  $\mu\text{m}$ .

#### 10 Optional ingredients

Optional ingredients in compositions of this invention can include deodorants, for example at a concentration of up to about 10% w/w. Suitable deodorant actives can comprise deodorant effective concentrations of antiperspirant metal salts, deoperfumes, and/or microbicides, including particularly bactericides, such as chlorinated aromatics, including biguanide derivatives, of which materials known as Irgasan DP300 <sup>TM</sup> (Triclosan), Tricloban <sup>TM</sup>, and Chlorhexidine warrant specific mention. A yet another class comprises biguanide salts such as available under the trade mark Cosmosil <sup>TM</sup>.

25 Other optional ingredients include wash-off agents, often present in an amount of up to 10% w/w to assist in

the removal of the formulation from skin or clothing.  
Such wash-off agents are typically nonionic surfactants  
such as esters or ethers containing a C<sub>8</sub> to C<sub>22</sub> alkyl  
moiety and a hydrophilic moiety which can comprise a  
5 polyoxyalkylene group (POE or POP) and/or a polyol.

A further optional constituent of the formulation  
comprises one or more secondary structurants which can be  
employed in addition to the esterified saccharide which  
10 is the primary structurant. The amount of such secondary  
structurants in the formulation is often zero, and  
usually not more than 15% of the formulation. It is  
normally not greater than the amount of the primary  
structurant.

15

The secondary structurants employable herein can be  
non-polymeric or polymeric. Solid linear fatty alcohol  
and/or a wax may be included but are not preferred. Non-  
polymeric secondary structurants, perhaps gelling agents  
20 of lower gel formation enthalpy, can be included.  
Gellants can comprise dibenzylidene alditols, e.g.  
dibenzylidene sorbitol. Further suitable gellants can  
comprise lanosterol, selected N-acyl amino acid  
derivatives, including ester and amide derivatives, such  
25 as N-lauroyl glutamic acid dibutylamide, which gellants  
can be contemplated in conjunction with 12-hydroxy

stearic acid or an ester or amide derivative thereof.  
Still further gellants include amide derivatives of di or  
tribasic carboxylic acids, such as alkyl N,N'  
dialkylsuccinamides, e.g. dodecyl N,N'-  
5 dibutylsuccinamide.

Polymeric structurants which can be employed can  
comprise organo polysiloxane elastomers such as reaction  
products of a vinyl terminated polysiloxane and a cross  
10 linking agent or alkyl or alkyl polyoxyalkylene-  
terminated poly (methyl substituted) or poly (phenyl  
substituted) siloxanes. A number of polyamides have also  
been disclosed as structurants for hydrophobic liquids.  
Polymers containing both siloxane and hydrogen bonding  
15 groups, which might be used as secondary structurants,  
have been disclosed in WO 97/36572 and WO 99/06473. If  
an aqueous disperse phase is present, Polyacrylamides,  
polyacrylates or polyalkylene oxides may be used to  
structure or thicken this aqueous phase.

20

The compositions herein can incorporate one or more  
cosmetic adjuncts conventionally contemplatable for  
antiperspirant solids or soft solids. Such cosmetic  
adjuncts can include skin feel improvers, such as talc or  
25 finely divided polyethylene, for example in an amount of  
up to about 10%; skin benefit agents such as allantoin or



lipids, for example in an amount of up to 5%; colours;  
skin cooling agents other than the already mentioned  
alcohols, such as menthol and menthol derivatives, often  
in an amount of up to 2%, all of these percentages being  
5 by weight of the composition. A commonly employed  
adjunct is a perfume, which is normally present at a  
concentration of from 0 to 4% and in many formulations  
from 0.25 to 2% by weight of the composition.

10 Translucent/Transparent Compositions

If a composition of this invention is formulated as  
an emulsion it is possible to construct the formulation  
such that the emulsion is translucent or transparent. In  
15 order to do this the refractive indices of the water-  
immiscible continuous phase and the polar or aqueous  
disperse phase must be matched to each other and the  
value of refractive index at which they are matched must  
also approximately match the refractive index of the  
20 structurant.

The refractive index of a fibrous network of a  
structurant can be determined by using that structurant  
to gel a number of oils or oil mixtures of differing  
25 refractive index. When the resulting gel is transparent,  
the refractive index of the oil or oil mixture (which can

be determined by conventional measurement, is a good approximation to the refractive index of the structurant.

The oils or mixtures or oils should be chosen from these which are gelled well by the structurant to avoid  
5 interfering effects. When the gel is not transparent, but is translucent, it will indicate a refractive index which is not precisely matched to the refractive index of the structurant, and thus indicate an amount of mismatch which can be tolerated without loss of translucency. It  
10 is likely that the matched refractive indices of the liquid phases will be not over 0.07 units below and not over 0.04 units above the refractive index of the structurant.

15 Using this method we have determined the refractive index of a preferred structurant, namely cellobiose octa-nanoate, to fall in a range between 1.45 and 1.50, being approximately 1.48 at 22°C. With this structurant we have found that the value at which the refractive  
20 indices of the continuous and disperse phases are matched can be somewhat below the refractive index of the structurant, down to a value of 1.42 or even down as far as 1.41 or 1.40. A value slightly above 1.48 would be useable also, but is inconvenient to achieve.

25

For the continuous phase, silicon-free water-

immiscible liquid oils generally have refractive indices in a range from 1.43 to 1.49 at 22°C and can be used alone or mixed together to give a silicon-free carrier liquid with refractive index in this range. Volatile  
5 silicone oils generally have a refractive index slightly below 1.40 at 22°C, but carrier liquid mixtures with refractive indices in the range from 1.41 to 1.46 can be obtained by mixing volatile silicone with other oils. Non-volatile silicone oils generally have refractive  
10 indices in a range from 1.45 to 1.48 at 22°C and so can be included when desired.

The refractive index of the continuous phase will be very close to the refractive index of the carrier liquid  
15 (usually a carrier liquid mixture) which is its principal component.

For the disperse phase, a solution of an antiperspirant active salt in water alone will generally  
20 display a refractive index below 1.425. The refractive index can be raised by incorporating a diol or polyol into the aqueous solution. It is believed to be novel to match the refractive index of a polar disperse phase to that of a structurant network within a continuous phase.  
25 Moreover, it can be achieved without using so much diol or polyol as will make the composition excessively

sticky.

If composition of this invention is a gelled continuous phase without any disperse phase, it can be  
5 made transparent or translucent by approximating the refractive index of the liquid carrier to that of the esterified saccharide structurant in the manner discussed above.

10 For a composition which is a suspension the route to a transparent or translucent composition is to match the refractive indices of the liquid carrier and the suspended solid to that of the esterified saccharide. Particulate antiperspirant actives which are anhydrous  
15 solids generally have a refractive index substantially above 1.50 which is brought down by hydration, but we have found that it is not easy to obtain an antiperspirant active with a refractive index of 1.48 or below even if the active is partially hydrated to lower  
20 its refractive index.

For this reason, a feature within this invention is to prefer the emulsion form of antiperspirant stick when seeking to achieve a transparent or translucent product.

25

For the regular production of compositions with

optimum transparency it may prove desirable to monitor  
the refractive indices of the raw materials to detect any  
batch to batch variation. If necessary the composition  
of a liquid phase can be adjusted by variation of the  
5 quantity of a constituent material.

#### Properties and Product Packages

The compositions of this invention are structured  
10 liquids and may be firm or soft in appearance. Even a  
soft solid has an ability to sustain its own shape, for  
instance if it is removed from a mould without being  
subjected to shear it will retain its shape for at least  
30 seconds, usually longer.

15

A composition of this invention will usually be  
marketed as a product comprising a container with a  
quantity of the composition therein, where the container  
has at least one aperture for the delivery of  
20 composition, and means for urging the composition in the  
container towards the delivery aperture. Conventional  
containers take the form of a barrel of oval cross  
section with the delivery aperture(s) at one end of the  
barrel.

25

A composition of this invention may be sufficiently rigid that it is not apparently deformable by hand pressure and is suitable for use as a stick product in which a quantity of the composition in the form of a  
5 stick is accommodated within a container barrel having an open end at which an end portion of the stick of composition is exposed for use. The opposite end of the barrel is closed.

10 Generally the container will include a cap for its open end and a component part which is sometimes referred to as an elevator or piston fitting within the barrel and capable of relative axial movement along it. The stick of composition is accommodated in the barrel between the  
15 piston and the open end of the barrel. The piston is used to urge the stick of composition along the barrel. The piston and stick of composition may be moved axially along the barrel by manual pressure on the underside of the piston using a finger or rod inserted within the  
20 barrel. Another possibility is that a rod attached to the piston projects through a slot or slots in the barrel and is used to move the piston and stick. Preferably the container also includes a transport mechanism for moving the piston comprising a threaded rod which extends  
25 axially into the stick through a correspondingly threaded aperture in the piston, and means mounted on the barrel

for rotating the rod. Conveniently the rod is rotated by means of a handwheel mounted on the barrel at its closed end, i.e. the opposite end to the delivery opening.

- 5        If a composition of this invention is softer, but still capable of sustaining its own shape it will be more suited for dispensing from a barrel with a closure instead of an open end, where the closure has one or more apertures through which composition from the barrel can  
10 be extruded. The number and design of such apertures is at the discretion of the designer of the package.

The component parts of such containers are often made from thermoplastic materials, for example  
15 polypropylene or polyethylene. Descriptions of suitable containers, some of which include further features, are found in US patents 4865231, 5000356 and 5573341.

#### Measurement of Properties

- 20 i) Penetrometer

The hardness and rigidity of a composition which is a firm solid can be determined by penetrometry. If the composition is a softer solid, this will be observed as a substantial lack of any resistance to the penetrometer  
25 probe.

A suitable procedure is to utilise a lab plant PNT penetrometer equipped with a Seta wax needle (weight 2.5 grams) which has a cone angle at the point of the needle specified to be  $9^{\circ}10' \pm 15'$ . A sample of the composition with a flat upper surface is used. The needle is lowered onto the surface of the composition and then a penetration hardness measurement is conducted by allowing the needle with its holder to drop under a total weight, (i.e. the combined weight of needle and holder) of 50 grams for a period of five seconds after which the depth of penetration is noted.

Desirably the test is carried out at a number of points on each sample and the results are averaged. Utilising a test of this nature, an appropriate hardness for use in an open-ended dispensing container is a penetration of less than 30 mm in this test, for example in a range from 2 to 30 mm. Preferably the penetration is in a range from 5mm to 20 mm.

20

In a specific protocol for this test measurements on a stick were performed in the stick barrel. The stick was wound up to project from the open end of the barrel, and then cut off to leave a flat, uniform surface. The needle was carefully lowered to the stick surface, and

25



then a penetration hardness measurement was conducted. This process was carried out at six different points on the stick surface. The hardness reading quoted is the average value of the 6 measurements.

5

ii) Texture analyser

The hardness of a softer solid can be measured by using a texture analyser. This test apparatus can move a blunt probe into or out from a sample at a controlled speed and at the same time measure the applied force. The parameter which is determined as hardness is a function of the peak force and the projected area of indentation.

15 A specific test protocol used a Stable Micro systems TA.XT2i Texture Analyser. A metal sphere, of diameter 9.5mm, was attached to the underside of the Texture Analyser's 5 kg load cell such that it could be used for indenting a sample placed beneath it on the base plate of the instrument. After positioning the sample, the sphere position was adjusted until it was just above the sample surface. Texture Expert Exceed software was used to generate the subsequent motion profile used in the test method. This profile initially indented the sphere into 20 the sample at an indentation speed of 0.05mm/s until a designated force was reached, which was chosen such that 25

the distance of penetration into the sample was less than the radius of the sphere. At this load the direction of motion of the sphere was immediately reversed to withdraw the sphere from the sample at the same speed of 0.05mm/s.

- 5 During the course of the test, the data acquired were time(s), distance (mm) and force (N) and the data acquisition rate was 25 Hz.

- Suitable samples for measurement were either
- 10 contained in stick barrels, which had a screw mechanism, or in 15 ml glass jars. For the barrel samples, the stick was wound up until it protruded above the edges of the barrel and then a knife was used to skim the top of the barrel in such a way as to leave a flat uniform
- 15 surface. The stick was then pushed back into the barrel as far as possible to minimise any mechanical interference resulting from the compliance of the screw mechanism in the pack. Two indents were generally made either side of the screw. The samples in the 15 ml jars
- 20 needed no surface preparation but only had enough surface area for a single indentation test to be performed.

The data associated with each test were manipulated using standard spreadsheet software and used to calculate the hardness,  $H$ , using the following equation:

$$H[N/mm^2] = \frac{F_{max}[N]}{A_p[mm^2]}$$

where  $F_{max}$  is the peak load and  $A_p$  is the projected area of the indentation remaining on unloading. This area can be calculated geometrically from the plastic indentation depth. This is slightly less than the total penetration depth measured under load because of elastic deformation of the sample. The plastic indentation depth is calculated from a graph of the unloading-force-versus-total-penetration-depth. The initial slope of this unloading data depends on the initial elastic recovery of the sample. The plastic indentation depth is estimated from an intercept between the zero force axis and a straight line drawn at a tangent to the initial part of the unloading slope.

Similar hardness measurements were also done using a desktop Instron Universal Testing Machine (Model 5566) fitted with a 10 N load cell, and the data analysis performed in the same way.

iii) Deposition and whiteness of deposit

Another test of the properties of a composition is the amount of the composition which is delivered onto a surface when the composition is drawn across that surface (representing the application of a stick product to human

skin). To carry out this test of deposition, a sample of the composition with standardised shape and size is fitted to apparatus which draws the sample across a test surface under standardised conditions. The amount transferred to the surface is determined as an increase in the weight of the substrate to which it is applied. If desired the colour, opacity or clarity of the deposit may subsequently be determined.

10 A specific procedure for such tests used apparatus to apply a deposit from a stick onto a substrate under standardised conditions and then measures the mean level of white deposits using image analysis.

15 The substrates used were

a: 12 x 28cm strip of grey abrasive paper (3M™ P800 WetorDry™ Carborundum paper)

b: 12 x 28cm strip of black Worsted wool fabric.

20 The substrates were weighed before use. The sticks were previously unused and with domed top surface unaltered.

The apparatus comprised a flat base to which a flat substrate was attached by a clip at each end. A pillar having a mounting to receive a standard size stick barrel

was mounted on an arm that was moveable horizontally across the substrate by means of a pneumatic piston.

Each stick was kept at ambient laboratory  
5 temperature overnight before the measurement was made.  
The stick was advanced to project a measured amount from the barrel. The barrel was then placed in the apparatus and a spring was positioned to biased the stick against the substrate with a standardised force. The apparatus  
10 was operated to pass the stick laterally across the substrate eight times. The substrate was carefully removed from the rig and reweighed.

#### Whiteness of Deposit

15 The deposits from the previous test were assessed for their whiteness after an interval of 24 hours approximately.

This was done using a Sony XC77 monochrome video  
20 camera with a Cosmocar 16mm focal length lens positioned vertically above a black table illuminated from a high angle using fluorescent tubes to remove shadowing. The apparatus was initially calibrated using a reference grey card, after the fluorescent tubes had been turned on for  
25 long enough to give a steady light output. A cloth or Carborundum paper with a deposit thereon from the

previous test was placed on the table and the camera was used to capture an image. An area of the image of the deposit was selected and analysed using a Kontron IBAS image analyser. This notionally divided the image into a large array of pixels and measured the grey level of each pixel on a scale of 0 (black) to 255 (white). The average of the grey intensity was calculated. This was a measure of the whiteness of the deposit, with higher numbers indicating a whiter deposit. It was assumed that low numbers show a clear deposit allowing the substrate colour to be seen.

It has been found desirable to carry out deposition of a standard stick composition, and determine the whiteness of the deposit as a control.

iv) Light transmission

The translucency of a composition may be measured by placing a sample of standardised thickness in the light path of a spectrophotometer and measuring transmittance, as a percentage of light transmitted in the absence of the gel.

We have carried out this test using a dual-beam spectrophotometer. The sample of composition was poured not into a 4.5 ml cuvette made of polymethylmethacrylate

(PMMA) and allowed to cool to an ambient temperature of 20-25°C. Such a cuvette gives a 1 cm thickness of composition. Measurement was carried out at 580 nm, with an identical but empty cuvette in the reference beam of the spectrophotometer, after the sample in the cuvette had been held for 24 hours. We have observed that a composition which gives a transmittance of as little as 1% in this test is perceived by eye as "translucent". If a stick is made from a composition with 3% transmittance, it is possible to see cavities made by boring beneath the surface of the sample. By contrast, a conventional stick structure with stearyl alcohol is so opaque that it is impossible to see beneath its surface. A transmittance measured at any temperature in the range from 20-25°C is usually adequately accurate, but measurement is made at 22°C if more precision is required. In a number of preferred examples we have achieved a transmittance of 20% or above.

## 20 Preparation

Compositions of this invention can be produced by conventional processes for making suspension or emulsion solids or soft-solids. Such processes involve forming a heated mixture of the composition at a temperature which is sufficiently elevated that all the esterified

saccharide structurant dissolves, pouring that mixture into a mould, which may take the form of a dispensing container, and then cooling the mixture whereupon the structurant solidifies into a network of interconnected  
5 fibres extending through the water-immiscible liquid phase.

A convenient process sequence for a composition which is a suspension comprises first forming a solution  
10 of the esterified saccharide structurant in the water-immiscible liquid. This is normally carried out by agitating the mixture at a temperature sufficiently high that all the structurant dissolves (the dissolution temperature) such as a temperature in a range from 50 to  
15 120°C. Thereafter the particulate constituent, for example particulate antiperspirant active, is blended with the hot mixture. This must be done slowly, or the particulate solid must be preheated, in order to avoid premature gelation. The resulting blend is then  
20 introduced into a dispensing container such as a stick barrel. This is usually carried out at a temperature 5 to 30°C above the setting temperature of the composition.

The container and contents are then cooled to ambient temperature. Cooling may be brought about by nothing more  
25 than allowing the container and contents to cool. Cooling may be assisted by blowing ambient or even



refrigerated air over the containers and their contents.

In a suitable procedure for making emulsion formulations, a solution of the esterified structurant in the water-immiscible liquid phase is prepared at an elevated temperature just as for suspension sticks. If any emulsifier is being used, this is conveniently mixed into this liquid phase. Separately an aqueous or hydrophilic disperse phase is prepared by introduction of antiperspirant active into the liquid part of that phase (if this is necessary; antiperspirant actives can sometime be supplied in aqueous solution which can be utilised as is). This solution of antiperspirant active which will become the disperse phase is preferably heated to a temperature similar to that of the continuous phase with structurant therein, but without exceeding the boiling point of the solution, and then mixed with the continuous phase. Alternatively, the solution is introduced at a rate which maintains the temperature of the mixture. If necessary a pressurised apparatus could be used to allow a higher temperature to be reached, but with the structurant materials of this invention this is usually unnecessary. After the two phases are mixed, the resulting mixture is filled into dispensing containers, typically at a temperature 5 to 30°C above the setting temperature of the composition, and allowed to cool as

described above for suspension sticks.

### EXAMPLES

- 5        The examples below were prepared using a number of materials set out with their proprietary names in the following list. All temperature are in degrees Celsius. Refractive indices were measured at 25°C.
- 10    1)        octamethyl cyclotetrasiloxane (Volatile cyclic silicone also known as a cyclomethicone; DC 245 from Dow Corning)
- 2)        decamethyl cyclopentasiloxane (Volatile cyclic silicone also known as a cyclomethicone; DC 345 from Dow Corning)
- 15        3 & 4)      Non-volatile silicone fluids  
              DC 556 and DC 710 (Dow Corning)
- 5)        Polydecene (Silkflo 364NF from Albemarle)
- 6)        Isostearyl Alcohol (abbreviated to ISA -  
20        Prisorine 3515 from Unichema)
- 7)        C12-15 alkyl benzoate (Finsolv TN from Fintex)
- 8)        Mineral Oil (Sirius M70 from Dalton)
- 9)        Polypropyleneglycol 14 butylether (Fluid AP from Amercol)
- 25    10)        Isopropyl myristate (abbreviated to IPM from Unichema)

- 11) Isohexadecane (Permethyl 101A from Presperse Inc)
- 12) Isoeicosane (Permethyl 102A from Presperse Inc)
- 5 13) Cetyl dimethicone copolyol (Abil EM90 emulsifier from Th. Goldschmidt)
- 14) Al/Zr Tetrachlorohydrex glycine complex (AZAG 7167 from Summit)
- 15) 50% aqueous solution of Al/Zr pentachlorohydrate (Zirkonal 50 from Giuliani)
- 10 16) Al/Zr Tetrachlorohydrex glycine complex 30% in propylene glycol (WA2Z 8106 from Westwood)
- 17) Al/Zr tetrachlorohydrex glycine complex (AZG 375 from Summit)
- 15 18) Glycerol (from Aldrich)
- 19) Propylene glycol (from Fisons)
- 20) N-lauryl-L-glutamic acid di-n-butylamide (GP-1 from Ajinomoto)
- 21) 12-hydroxystearic acid (from Caschem)
- 20 22) Activated aluminium chlorohydrate - abbreviated to AACH (A-418 from Summit)
- 23) Bis-phenylpropyldimethicone, a non-volatile silicone fluid (SF 1555 from G E Silicones)
- 24) Polyglyceryl polyricinolate (Quest PGPR)
- 25 25) 1-octyldecanol (Eutanol G from Henkel/Cognis)
- 26) Hydrogenated polyisobutene (Panalene-L-14E from

**SUBSTITUTE SHEET (RULE 26)**

Amoco)

- 27) Hydrogenated polyisobutene (Fancol 800 from Fanning Corporation)
- 28) Polyglyceryl-3-diisostearate (Lameform TGI from  
5       Henkel/Cognis)
- 29) Polyglyceryl-2-dipolyhydroxystearate (Dehymuls PGPH  
      from Henkel/Cognis)
- 30) Polyalpha Olefins (Puresyn 4 from Mobil Chemical)
- 31) Ceteareth 20 (Eumulgin B2 from Henkel)
- 10 32) C20 - C40 alcohols (Unilin 425 from Petrolite)

**Example 1**

The enthalpy of gelation was measured for four structuring agents in three liquids. In each case the  
5 gels are made to contain 7 to 7.5 wt% of the structurant in the liquid.

A sample gel, weighing between 18 and 22 mg was placed in a stainless steel calorimeter capsule, which was  
10 sealed with an elastomeric O-ring. The capsule was placed in the DSC at room temperature and heated at 10K/minute to 150°C, held at 150°C for 60 seconds and cooled at 2K/minute to -50°C.

15 The procedure was repeated with DC 345 alone. The data recorded for DC 345 was subtracted from the data for the gel, so that the gel formation appears a departure from a flat baseline. The gelation enthalpy was calculated as the area between the peak and the baseline.

20

Values of enthalpy (in kJ/mole) were obtained as set out in the following table

Structurant	Liquid		
	DC 345	DC 345:ISA (80:20 ratio by weight)	Isostearyl alcohol (ISA)
$\alpha$ -cellobiose octa- octadecanoate		360	
$\alpha$ -cellobiose octa- dodecanoate		108	
$\alpha$ -cellobiose octa- undecanoate		117	
$\alpha$ -cellobiose octa- decanoate	84.7	94.6	
$\alpha$ -cellobiose octa- nonanoate	65	58	77
$\alpha$ -cellobiose octa- octanoate		57.8	
12-hydroxystearic acid		40	
$\beta$ -sitosterol and oryzanol (1:1 mole ratio)		22	
N-lauroyl glutamic acid di-n-butylamide (GP-1)		11	25
lanosterol	27	7	

**Example 2 (Comparative)**

Gels were prepared with lanosterol by a standard procedure in which the ingredients of the gel were placed in a 30ml glass bottle together with a magnetic stirrer bar. The mixture was stirred and heated until all the lanosterol had dissolved. The bottle was then removed from the heat, the stirrer bar taken out and the contents of the jar left to cool to room temperature.

10

The following was observed:

Lanosterol was found to dissolve at 10.0 wt% in Finsolv TN at 83°C. After cooling to room temperature for 1 hours a hard, transparent gel was obtained. However the gel was found to be unstable at room temperature: large crystalline lumps appeared within hours and spread throughout the entire gel leading to its collapse.

20      Lanosterol was found to dissolve at 5.0 wt% in 80:20 (wt%) DC 345: Finsolv TN at 85°C. After cooling to room temperature for 1 hour a hard, translucent gel was obtained. However the gel was found to be unstable at room temperature: large crystalline lumps developed after 25      1 week.

**Example 3 (Comparative)**

An unsuccessful attempt was made to prepare compositions as set out in the table below, using  
5 N-lauroyl glutamic acid di-n-butylamide (GP-1) as structurant

Compositions 3.1 and 3.2 would have been suspensions of solid antiperspirant active.

10

Compositions 3.3 and 3.4 would have been emulsions where the disperse phase would be a solution of antiperspirant active in water (Zirkonal 50 is a 50% aqueous solution of antiperspirant active).



Example no	3.1	3.2	3.3	3.4
	Suspension	Suspension	Emulsion	Emulsion
<b>Continuous phase</b>				
GP-1 (20)	6%	5%	3.5%	5%
DC 345 (2)	30%	53%	39%	43%
Isopropyl myristate (10)	44%	-	-	-
Isostearyl alcohol (6)	-	-	-	11%
Finsolv TN (7)	-	22%	16.5%	-
Abil EM90 (13)	-	-	1%	1%
<b>Disperse Phase</b>				
AZAG 7167 (14)	20%	20%	-	-
Zirkonal 50 (15)	-	-	40%	40%
<b>Continuous Phase Data</b>				
Temp at which all the GP-1 had dissolved	113°C	123°C	122°C	119°C
Temperature at which the continuous phase gelled	108°C	115°C	116°C	99°C

In each case the components of the continuous phase  
 5 were placed in a beaker and the mixture heated with  
 stirring on a hot plate until all the GP-1 structurant

**SUBSTITUTE SHEET (RULE 26)**

dissolved. The temperature at which it dissolved is shown in the table above.

---

The intention was then to cool the mixture, while  
5 still stirring gently to about 85-90°C in order to add  
the components of the disperse solid or liquid phase. In  
all cases the continuous phase gelled at a temperature  
(shown in the table) above or very close to 100°C, which  
was too high for safe addition of the disperse phase in  
10 an open laboratory.

Safe preparation at this high temperature would have  
required special measures such as pressurised apparatus.

**Example 4 (Comparative)**

Suspension sticks were prepared containing 12-hydroxystearic acid as structurant. The compositions are  
5 given in the following table

Example No	4.1	4.2
Continuous Phase		
12-hydroxystearic acid (21)	5%	7.5%
Finsolv TN (7)	75%	72.5%
Disperse Phase		
AACH (A-418 from Summit) (22)	20%	20%
Data		
Temperature for dissolution of 12-Hydroxystearic acid in the Finsolv TN	58°C	63°C
Gelling temperature of stick	41°C	47°C
Stick Hardness after 24 hours (penetrometer [mm])	12.6	11.2
Stick Hardness after 1 week storage at 22°C (penetrometer [mm])	13.8	12.0

The components of the continuous phase were placed in a beaker and the mixture heated with stirring on a hot  
10 plate until all the 12-hydroxystearic acid structurant dissolved. The temperature at which it dissolved is shown in the table above.

The mixture was then allowed to cool slightly, to about 10°C above the gelling temperature shown in the table, while stirring gently. The solid antiperspirant active was mixed in under low shear.

5

The resulting mixture was poured into stick barrels and allowed to cool to ambient laboratory temperature. In each case the mixture gelled to a rigid stick.

10

The hardness of the stick was determined by penetrometer after 24 hours at ambient temperature and then after storage at ambient temperature for 1 week. The results, in the table above show slight softening during storage. After the period of storage the sticks were

15

observed to have leaked some of the Finsolv TN solvent, which could be seen as free liquid on the stick surface.

Example 5

Cellobiose was esterified with nonanoic acid to  
yield the fully esterified product in the form of its  
5  $\alpha$ -anomer following a procedure generally as described in  
Takada et al, Liquid Crystals, Volume 19, page 441 (1995).

The following materials were used:

- 10  $\beta$ -D-cellobiose, 20 grams, 0.058 moles
- Nonanoic acid, 591.6 grams, 3.74 moles
- Trifluoroacetic anhydride, 297.6 grams, 1.42 moles.

These materials were obtained from Acros Organics -  
15 Fisher Scientific.

Into a 2 litre flange pot equipped with an overhead  
stirrer, water condenser and addition inlet was placed  
the nonanoic acid together with the trifluoroacetic  
20 anhydride. The resultant clear mixture was stirred up  
and heated to 100°C using a silicone oil bath and  
temperature probe. During heating it was noted that the  
colour of the reaction mixture darkened and developed a  
dark brown tinge. After allowing the mixture to stir for  
25 one hour at 100°C, the cellobiose was slowly added via a  
solid powder funnel to the dark activated solution, and a

dirty brown suspension was formed which re-dissolved forming a clear black solution within 10-20 minutes.

The reaction flask was then maintained at 100°C for a total of 6 hours then cooled down to ambient laboratory temperature. Next the contents of the flask were transferred into 2 litres of methanol containing 10% de-ionised water in an ice-cooled 5 litre beaker. Immediately an off-white solid precipitate came out of solution, this was filtered off and collected. The crude solid was recrystallised a total of 4 times from a tetrahydrofuran/methanol solution producing a white solid product.

The product was obtained in a quantity of 31.5 g which was a 37% yield. It had a melting point of 110°C. The infra-red spectrum showed an absorption peak at 1739  $\text{cm}^{-1}$  for the ester carbonyl group. The amount of free acid could be determined from its absorption peak at 1705  $\text{cm}^{-1}$ .

The n.m.r. spectrum showed the amount of cellobiose which was fully esterified to be 93.5% and showed the proportions of product which were the  $\alpha$ - and  $\beta$ -anomers, (93.5%  $\alpha$ -anomer).

Other esters of cellobiose were prepared in the same way. Samples of esterified cellobiose prepared as above were used to gel various water-immiscible liquids and mixtures of liquids. The procedure was as follows:

5

0.5 grams esterified cellobiose and 9.5 grams of the liquid (or other proportions to give a total of 10 grams) were weighed directly into a 15 gram or 30 gram glass jar. A small magnetic follower was placed in the jar  
10 which was then placed on a hot plate. It was stirred and heated until all of the esterified cellobiose had dissolved in the liquid. This "dissolution temperature" was noted. The jar was then removed from the hot plate, the stirrer was removed from the hot liquid in the jar.  
15 A thermometer was placed in the liquid and the contents of the jar were then left undisturbed to cool. The gelling temperature, i.e. the temperature at which the contents gelled, was noted. The jar was left to stand for 24 hours and then the contents of the jar were  
20 inspected visually, pressed with a probe and classified qualitatively according to their appearance as a soft, medium or hard gel. The clarity or otherwise of the gel was noted. In most instances the gel was remelted, the remelting temperature was noted, and some of the melt was  
25 poured into a plastic (polymethylmethacrylate) cuvette and allowed to cool back to ambient laboratory

temperature so that the gel reformed in the cuvette. The transmittance of light through the 1cm thickness of gel in the cuvette was determined at a wave length of 580 nm using an ultraviolet/visible spectrophotometer.

5

The following tables show the water-immiscible liquids which were used, the percentage of esterified cellobiose structurant used to gel the liquid, the dissolution temperature, the gelling temperature, the visual appearance of the gel, the remelt temperature and the percentage light transmittance (denoted as %T) through 1cm of the gel at 580nm.

Gelling with $\alpha$ -cellobiose octa-octanoate("CB8" R = $\text{COC}_7\text{H}_{15}$ )						
Liquid	% CB8	Diss Temp	Gel Temp	Remelt Temp	% T	Visual appearance of gel
ISA (6)	5	41	30	41		Hard & transparent -> crystal growth
	10	41	35			Hard & translucent -> crystal growth
DC 345 (2)	5	48	41	50	17	Hard & transparent/ translucent
	10	53	50			Hard & opaque
DC 556 (3)	5	48	30	45	49	Hard & transparent
	10	49	35			Hard & transparent
Silkflo 364 NF (5)	5	53	45	51	22	Hard & transparent
	10	55	50			Hard & opaque



Gelling with $\alpha$ -cellobiose octa-nonanoate ("CB9")						
Liquid	% CB9	Diss Temp	Gel Temp	Remelt Temp	% T	Visual appearance of gel
ISA (6)	5	57	25	46	78	Medium/hard & transparent
DC 345 (2)	5	62	42	60	15	Hard & transparent/translucent
DC 566 (3)	5	69	29	52	81	Hard & transparent
Silkflo 364NF (5)	5	71	40	55	78	Hard & transparent
Fluid AP (9)	5	82	38	55	37	Soft/medium & transparent
DC 345 : Fluid AP 80 : 20 wt ratio	5	68	28	54	39	Soft/medium & transparent
DC 710 (4)	5	82	48	62	11	Medium & translucent
DC 710 : DC 345 60 : 40 wt ratio	5	74	33	60	4	Hard & translucent

It can be seen from the above table that the gelation temperatures were low. The remelt temperatures were well below 80°C and the compositions could be prepared without any need to exceed 85°C.

Gelling with $\alpha$ -cellobiose octa-decanoate ("CB10" R = $\text{COC}_9\text{H}_{19}$ )						
Liquid	% CB10	Diss Temp	Gel Temp	Remelt Temp	% T	Visual appearance of gel
Finsolv TN (7)	5	72	25	38		Very soft & transparent gel
ISA (6)	5	72	25	47	46	Medium & transparent
	7	68	25	52		Hard & translucent
	10	76	30			Medium & transparent
DC 345 (2)	5	85	62	71	0.02	Hard & translucent/ opaque
	7	84	65	59		Hard & opaque
DC 556 (3)	3	79	46	59		Medium & transparent
	5	n/d	50	52	2	Medium/hard & translucent
	7	74	40	67		Hard & translucent
Fluid AP (9)	3	85	35	60		Medium & transparent
	5	82	33	51		Medium & transparent
	7	78	51	53	3	Medium & translucent
	10	84	45			Medium & translucent/ opaque
DC 345 : Fluid AP 80 : 20 wt ratio	5	73	25	55	<0.0 1	Medium & translucent/ opaque
	7	82	36	49		Hard & opaque
	10	83	41			Hard & opaque
DC 710 (4)	5	100	80	80	0.15	Medium & opaque
DC 710 : DC 345 60 : 40 wt ratio	5	92	65	65	1	Medium & translucent/opaque trans

Gelling with $\alpha$ -cellobiose octa-dodecanoate ("CB12" R = $\text{COC}_{11}\text{H}_{23}$ )						
Liquid	% CB12	Diss Temp	Gel Temp	Remelt Temp	% T	Visual appearance of gel
ISA (6)	5	54	30	48	12	Soft & transparent/trans-lucent
DC 345 (2)	5	50	48	50	0.17	Soft & opaque
DC 556 (3)	5	60	35	48	17	Medium & transparent/trans-lucent
Silkflo 364 NF (5)	5	53	45	55	3	Medium & transparent
Fluid AP (9)	5	63	43	55	4	Soft & transparent/translucent
DC 345: Finsolv TN 80 : 20 wt ratio	5	65	29	42	3	soft & translucent
DC 345 : Fluid AP 80 : 20 wt ratio	5	63	42	50	0.25	Soft/medium & opaque
DC 710 (4)	5	65	57	65	1	Medium & opaque
DC 710 : DC 345 60 : 40 wt ratio	5	65	48	55	39	Soft & transparent

Gelling with $\alpha$ -cellobiose octa-octadecanoate ("CB18" $R = \text{COC}_{17}\text{H}_{35}$ )						
Liquid	% CB18	Diss Temp	Gel Temp	Remelt Temp	% T	Visual appearance of gel
Finsolv TN (7)	5	68	47	60	0.12	very soft & opaque
	7	68	47			
IPM (10)	5	68	50	59	0.01	very soft & opaque
	7	72	50			very soft & opaque
ISA (6)	5	68	58	62	0.03	very soft & opaque
	7	70	61			soft & opaque
DC 345 (2)	5	85	82	80	<0.01	soft & opaque
	7	87	86			soft & opaque
	10	85	84			medium & opaque
DC 556 (3)	5	77	76	75	0.08	soft & opaque
	7	83	79			soft & opaque
	10	83	79			medium & opaque
Silkflo 364 NF (5)	5	72	66	75	0.11	medium & opaque
	7	72	68			medium & opaque
	10	79	69			medium & opaque
Fluid AP (9)	5	78	76	78	0.01	soft & opaque
	7	82	77			medium & opaque
	10	82	81			soft & opaque

Example 6

An antiperspirant suspension stick is prepared with the following formulation, using the same procedure as in  
5 Example 3

	Parts by weight
Cyclomethicone, DC 245 (1)	54.8
Polydecene (5)	13.7
Cellobiose octa-nonanoate	7.5
AZAG 7167 (14)	24

Example 7

Opaque emulsion sticks were prepared with formulations as set out in the table below.

5

To prepare these sticks, the cyclomethicone was mixed with the other organic liquids (if any) including the cetyl dimethicone copolyol which functioned as an emulsifier (silicone surfactant) and the mixture was  
10 heated with gentle stirring to a temperature 5 to 10°C above the temperature at which the structurant had been found to dissolve in a preliminary test. The esterified cellobiose was then added and allowed to dissolve.

15 The disperse phase (also referred to as internal phase) was an aluminium zirconium active dissolved in water or in a mixture of a polyol and water. This disperse phase was pre-heated to the same temperature as the organic oils containing the esterified cellobiose and  
20 added slowly to them over a period of one minute while mixing with a Silverson mixer. After addition was complete the formulation was mixed at higher speed for five minutes. Stirring speed was then reduced for a further one minute after which the mixture was poured into  
25 stick barrels and allowed to cool undisturbed to ambient laboratory temperature. The sticks were tested by penetrometer, by texture analyser and for whiteness of deposits, in each instance by the test procedures given earlier. All of the sticks were opaque although without

the chalky white appearance of a commercial white stick (CWS) structured with stearyl alcohol and castor wax whose test results are given at the right of the table.

Examples	7.1	7.2	7.3	CWS
	% by weight			
Cyclomethicone DC 245 (1)	18	22.25	21.7	
Polydecene (5)	22.75	27.5	27.4	
PPG-14 Butyl Ether (9)	4.5	5.5	5.4	
Cellobiose octa-nonanoate	3.75	3.75	4.5	
Cetyl Dimethicone Copolyol (13)	1	1	1	
Zirkonal 50 (15)	40	40	40	
Water	10	-	-	
	Properties			
penetration depth (mm)	16.8	17.5	15.7	9.8
Hardness by texture analyser (N/mm <sup>2</sup> )	0.11	0.10	0.12	-
Whiteness on grey paper 24 hours after deposition	19	16	16	118
Whiteness on black wool 24 hours after deposition	28	29	27	186

Example 8

The procedure of Example 7 was repeated to prepare a number of emulsion sticks with formulations set out in the following tables. The continuous and disperse phases were formulated to have refractive indices which matched closely at the value given in the tables. These sticks were tested as before and the properties are also given in these tables.



Examples	8.1	8.2	8.3	8.4	8.5	8.6
	% by weight					
Cyclomethicone DC245 (1)	22.625	18.75	25.5	19	26	17.75
Mineral Oil (8)	22.625	-	-	-	-	-
Polydecene (5)	-	22.5	15.75	22	15	22
PPG-14 Butyl Ether (9)	-	4	4	-	-	4.25
Isostearyl Alcohol (6)	-	-	-	4.25	4.25	-
Cellobiose octa-nonanoate	3.75	3.75	3.75	3.75	3.75	5
Cetyl Dimethicone Copolyol (13)	1	1	1	1	1	1
Zirkonal 50 (15)	40	40	40	40	40	40
Glycerol (18)	10	10	7.5	10	7.5	10
Water	-	-	2.5	-	2.5	-
Propylene glycol (19)	-	-	-	-	-	-
AZG 375 (17)	-	-	-	-	-	-
	Properties					
Matched refractive index of phases	1.43	1.43	1.425	1.435	1.425	1.43
penetration depth (mm)	19.3	18.5	17.3	24.7	23.6	12.4
Hardness by texture analyser (N/mm <sup>2</sup> )	0.11	0.12	0.08	0.07	0.06	0.17
Whiteness on grey paper 24 hours after deposition	-	15	16	18	19	16
Whiteness on black wool 24 hours after deposition	-	24	28	25	30	26
Transmittance at 580nm	-	38%	33%	41%	35%	51%

SUBSTITUTE SHEET (RULE 26)

Examples	8.7	8.8	8.9	8.10	8.11
	% by weight				
Cyclomethicone DC245 (1)	16.75	18	14.02	28.4	4.5
Cyclomethicone DC345 (2)					
Mineral Oil (8)	-	-	-	-	
Polydecene (5)	20.75	22.75	17.72	13.1	50.75
PPG-14 Butyl Ether (9)	4	4.5	3.51	3.75	-
Isostearyl Alcohol (6)	-	-	-	-	-
Cellobiose octa-nonanoate	7.5	3.75	3.75	3.75	3.75
Cetyl Dimethicone Copolyol (13)	1	1	1	1	1
Zirkonal 50 (15)	40	-	40	40	-
Glycerol (18)	10	4	17.5	6.25	12
Water	-	14	2.5	3.75	8
Propylene glycol (19)	-	12	-	-	-
AZG 375 (17)	-	20	-	-	20
	Properties				
Matched refractive index of phases	1.43	1.43	1.43	1.42	1.45
penetration depth (mm)	11	14.5	14.9	15.1	14.8
Hardness by texture analyser (N/mm <sup>2</sup> )	0.29	0.11	0.14	0.13	0.11
Whiteness on grey paper 24 hours after deposition	17	20	18	21	16
Whiteness on black wool 24 hours after deposition	25	28	25	31	19
Transmittance at 580nm	48%	82%	65%	30%	72%

SUBSTITUTE SHEET (RULE 26)

Examples	8.12	8.13	8.14	8.15	8.16
	% by weight				
Cyclomethicone DC245 (1)	41.85	35.4	10.04	10.64	6.96
Permethyl 101A (11)	2.15				
Permethyl 102A (12)	-	8.6			
Polydecene (5)			12.7	13.45	8.8
PPG-14 Butyl Ether (9)			2.51	2.66	1.74
Cellobiose octa-nonanoate	5	5	3.75	2.25	1.5
Cetyl Dimethicone Copolyol (13)	1	1	1	1	1
Zirkonal 50 (15)	40	40	52.71	52.71	60.24
Glycerol (18)	0.75	4.5	17.29	17.29	19.76
Water	9.25	5.5	-	-	-
	Properties				
Matched refractive index of phases	1.40	1.41	1.43	1.43	
penetration depth (mm)	13.5	13.2	12.0	16.8	
Hardness by texture analyser (N/mm <sup>2</sup> )	0.16	0.15	0.13	0.07	
Whiteness on grey paper 24 hours after deposition	59	61	24	24	
Whiteness on black wool 24 hours after deposition	122	24	14.9	16.2	
Transmittance at 580nm	2.7%	5%	33%	73%	

SUBSTITUTE SHEET (RULE 26)

Example 9

Sticks were prepared and tested in accordance with the procedure given in Example 7. The sticks were tested  
5 for hardness by texture analyser and/or by penetrometer. They were observed to give deposits of low whiteness, but numerical data were not recorded.

For some sticks in this example the refractive  
10 indices of the water-immiscible continuous phase and the polar antiperspirant active solution were matched sufficiently to give translucent sticks. Some values of transmittance are shown.

Examples	9.1	9.2	9.3	9.4	9.5
	% by weight				
DC245 (1)	44	21.625	21.625	21.625	18
Silkflo364 (5)	-	-	-	21.625	4
Permethyl 102A (12)	-	21.625	-	-	
SF1555 (23)	-	-	21.625	-	22
Abil EM90 (13)	1	-	-	-	1
Quest PGPR (24)		1.75	1.75	1.75	-
Esterified Cellobiose -C9	5	5	5	5	5
Zirkonal 50 (15)	39	40	40	40	40
Glycerol (18)	-	8	9	8.75	10
Water	11	2	1	1.25	
	Properties				
Penetration depth (mm)	9.3	12	11.3	13	
Hardness by texture analyser (N/mm <sup>2</sup> )	0.10	0.12	0.12	0.21	0.13

Examples	9.6	9.7	9.8	9.9	9.10
	% by weight				
Cyclomethicone DC 245 (1)	7.6	6.8	36.5	1.7	1.25
isostearyl alcohol (6)	-	-	-	23.3	-
octyldodecanol (25)	-	-	-	-	23.1
SF1555 (23)	37.43	37.7	7	-	-
Silkflo 364 (5)	-	-	-	16.8	17.65
Esterified Cellobiose -C10	8.12	7.3	7.8	7	7
Cetyl Dimethicone Copolyol (Abil EM90) (13)	1.1	1	1	1	1
Westwood active (16)	43.54	41	42	40	40
Glycerol (18)	-	4.7	5.2	6.8	6.5
Water	2.21	1.5	0.5	3.4	3.5
	Properties				
Matched RI of phases	1.45	1.45	1.46	1.45	1.45
penetration depth (mm)	9.1	6.9	8.7	8.8	9.1
Hardness by texture analyser (N/mm <sup>2</sup> )	0.37	0.03	0.08	0.04	0.19
Transmittance at 580nm (%)	8	3	5	6	5

**SUBSTITUTE SHEET (RULE 26)**

Examples	9.11	9.12	9.13	9.14
	% by weight			
DC245 (1)	12	11.32	-	-
Silkflo 364 (5)	32.5	30.68	39	41.5
Abil EM90 (13)	0.5	0.5	1	1
Esterified Cellobiose -C10	5	7.5	10	7.5
Zirkonal 50 (15)	33	33	-	-
Westwood active (16)	-	-	48.06	48.06
Glycerol (18)	17	17	-	-
water	-	-	1.94	1.94
	Properties			
penetration depth (mm)	19	14	7.3	9.6
Hardness by texture analyser (N/mm <sup>2</sup> )	0.44	0.07	0.47	0.15

Example 10

The procedure of Example 7 was repeated to prepare a number of emulsion sticks with formulations set out in the following tables. As in Example 8, the continuous and disperse phases were formulated to have refractive indices which matched closely at the value given in the tables. The sticks were tested for hardness by texture analyser and/or by penetrometer. They were observed to give deposits of low whiteness, consistent with their good clarity, but numerical data were not recorded.

The refractive indices of sample quantities of the water-immiscible liquid mixture and the antiperspirant active solutions were checked before making the sticks. If necessary their formulations were modified very slightly to optimise the refractive index match.



Examples	10.1	10.2	10.3	10.4	10.5	10.6
	% by weight					
Permethyl 102A (12)	41.36	-	-	-	-	-
Panalene L-14E (26)	-	-	22	-	-	-
Fanco 800 (27)	-	-	-	22	22	-
Puresyn 4 (30)	-	-	-	-	-	22
DC245 (1)	2.64	11.4	22	22	22	22
SF 1555 (23)	-	34.1	-	-	-	-
Esterified cellobiose C9	5	4.9	5	5	5	5
Abil EM90 (13)	1	1	1	1	1	1
Zirkonal 50 (15)	-	-	40	40	36.6	40
Westwood active (16)	50	48.6	-	-	-	-
Glycerol (18)	-	-	9.35	7.5	13.4	8.75
Water	-	-	0.65	2.5	-	1.25
	Properties					
Matched RI of phases (at 25°C)	1.46	1.45	1.431	1.425	1.437	1.429
penetration depth (mm)	9	11	10.5	12.1	7.9	8.8
Hardness by texture analyser (N/mm <sup>2</sup> )	0.11	0.11	0.13	0.12	0.11	0.10
Transmittance at 580nm (%)	68	70	40	6	70	37

Examples	10.7	10.8	10.9	10.10	10.11
	% by weight				
DC245 (1)	22	22.25	22.25	21.625	-
DC556 (3)	22				
Silkflo364 (5)		-	-	-	44
Permethyl 102A (12)	-	22.25	-	-	-
Panalene-L-14E (26)	-	-	-	21.625	-
SF1555 (23)	-	-	22.25	-	-
Abil EM90 (13)	1	0.5	0.5	-	1
Lameform TGI (26)	-	-	-	0.875	-
Dehymuls PGPH (27)	-	-	-	0.875	-
Esterified cellobiose C9	5	5	5	5	5
Zirkonal 50 (15)	40	40	40	40	50
Glycerol (18)	9	8	9	9.8	-
Water	1	2	1	0.2	
	Properties				
Matched RI of phases (at 25°C)	1.428	1.43	1.43	1.43	1.46
penetration depth (mm)	9.0	11	11	10.5	9
Hardness by texture analyser (N/mm <sup>2</sup> )	0.10	0.09	0.16	0.13	0.13
Transmittance at 580nm (%)	40	22	33	36	24

SUBSTITUTE SHEET (RULE 26)

Examples	10.12	10.13	10.14	10.15	10.16	10.17
	% by weight					
DC245 (1)	-	-	-	22	22	18
Silkflo364 (5)	44	-	-	-	-	5.3
Permethyl 102A (12)	-	44	-	22	-	-
Panalene-L-14E (26)	-	-	44	-	-	-
SF1555 (23)	-	-	-	-	22	-
Octyldodecanol (25)	-	-	-	-	-	21.9
Abil EM90 (13)	1	1	1	1	1	1
Esterified Cellobiose C9	5	5	5	5	5	5
Zirkonal 50 (15)	18	21.5	12	-	-	37.8
AZG-375 (17)	-	-	-	25	25	
Glycerol (18)	32	28.5	38	0.6	2.5	11
Water	-	-	-	24.4	22.5	
	Properties					
Matched refractive index of phases (at 25°C)	1.45	1.45	1.46	1.43	1.43	1.43
penetration depth (mm)	9	9	7	9	8	-
Hardness by texture analyser (N/mm <sup>2</sup> )	0.13	0.15	0.20	-	0.21	0.12
Transmittance at 580nm (%)	74	46	82	53	41	24

**SUBSTITUTE SHEET (RULE 26)**

**Example 11**

The procedure of Example 7 was used to prepare a number of emulsion sticks with formulations set out in the following table. These sticks did not contain antiperspirant active. They would be useful as moisturizing stick or lip salve and their compositions could be used as the basis for other, probably opaque, cosmetic stick products. The continuous and disperse phases were formulated to have refractive indices which matched closely at the values given in the table, but evaporative losses during processing interfered with this. The sticks were tested for hardness by texture analyser and/or by penetrometer.

Examples	11.1	11.2	11.3	11.4
	% by weight			
DC45 (1)	22	22	16.72	19.36
Silkflo364 (5)	22	-	27.28	-
SF1555 (23)	-	22	-	24.64
Abil EM90 (13)	1	1	1	1
Esterified Cellobiose C9	5	5	5	5
Glycerol (18)	33.5	37.5	-	-
Water	16.5	12.5	-	-
Propylene Glycol (19)	-	-	50	50
	Properties			
Matched RI of phases (at 25°C)	1.42	1.43	1.43	1.43
penetration depth (mm)	9	9	-	10
Hardness by texture analyser (N/mm <sup>2</sup> )	0.13	0.15	0.15	-

**SUBSTITUTE SHEET (RULE 26)**

Example 12

The procedure of Example 7 was used to prepare translucent emulsion sticks with the formulation below in which the structurant is  $\alpha$ -cellobiose octa-undecanoate ("CB11"). As in Example 8, the continuous and disperse phases were formulated to have refractive indices which matched closely at the value given. The sticks were tested for hardness by texture analyser and/or by penetrometer. They were observed to give deposits of low whiteness.

Ingredients	percent by weight
DC245 (1)	11
Silkflo 364 (5)	33
Abil EM90 (13)	1
Esterified Cellobiose C11	5
Zirkonal 50 (15)	33
Glycerol (18)	17
Properties	
Matched RI of phases (at 25°C)	1.44
penetration depth (mm)	16
Hardness by texture analyser (N/mm <sup>2</sup> )	0.05
Transmittance at 580nm (%)	6

Example 13

The procedure of Example 7 was used to prepare an opaque emulsion stick of the following formulation, which  
5 included agents to assist wash-off.

Ingredients	percent by weight
DC245 (1)	16.4
Silkflo 364 (5)	24.6
Abil EM90 (13)	1
Esterified cellobiose C9	5
Zirkonal 50 (15)	40
Glycerol (18)	10
Cetareth 20 (31)	2.5
C <sub>20-40</sub> alcohols (32)	0.5

CLAIMS:

1. A cosmetic composition comprising a water-immiscible carrier liquid and a structurant therefor which is  
5 effective to gel the composition upon cooling from a temperature at which the structurant is a mobile solution in the carrier liquid, characterised in that the structurant is an at least partially esterified saccharide which contains no more than eight monosaccharide residues  
10 and which structurant has an enthalpy of gelation in the carrier liquid with a magnitude of at least 45 kJ/mole.
  
2. A cosmetic composition comprising a water-immiscible carrier liquid and a structurant therefor which is  
15 effective to gel the composition upon cooling from a temperature at which the structurant is a mobile solution in the carrier liquid, characterised in that the structurant is an at least partially esterified saccharide which contains no more than eight monosaccharide residues  
20 and which structurant is able to gel an 80:20 wt% mixture of decamethyl cyclopentasiloxane and isostearyl alcohol with an enthalpy of gelation in at least one of the liquids with a magnitude of at least 45 kJ/mole.



3. A composition according to claim 1 or claim 2 wherein the esterified saccharide structurant contains from 2 to 5 monosaccharide residues.
- 5 4. A composition according to claim 3 wherein the esterified saccharide structurant is an esterified disaccharide.
- 10 5. A composition according to any one of claims 1 to 4 wherein the esterified saccharide structurant is esterified at a majority of the hydroxyl groups of the saccharide.
- 15 6. A composition according to any one the preceding claims wherein the esterified saccharide structurant contains esterifying acyl groups which contain an average of at least six carbon atoms.
- 20 7. A composition according to any one of the preceding claims wherein the composition is an emulsion with a hydrophilic, preferably water-miscible, disperse phase in addition to said water-immiscible liquid continuous phase.
8. A composition according to claim 7 wherein the disperse phase contains a diol or polyol.

9. A composition according to claim 7 or claim 8 which contains from 0.1% to 10% by weight of a nonionic emulsifier.
- 5 10. A composition according to any one of claims 1 to 9 which does not contain more than 8% by weight of ethanol or any monohydric alcohol with a vapour pressure above 1.3 kPa at 22°C.
- 10 11. A composition according to any one of claims 1 to 6 wherein the composition is a suspension with a particulate solid material disperse in said liquid carrier.
12. A composition according to any one of the preceding  
15 claims wherein the water-immiscible liquid carrier contains a volatile silicone and optionally a non-volatile silicone and/or a non-silicone hydrophobic organic liquid selected from hydrocarbons, hydrophobic aliphatic esters, aromatic esters, hydrophobic alcohols and hydrophobic ethers.
- 20 13. A composition according to any one of the preceding claims wherein the water-immiscible carrier liquid contains silicone oil in an amount which is at least 10% by weight of the composition.

14. A composition according to any one of the preceding claims containing from 0.1 to 12% by weight of the structurant.
- 5 15. A composition according to any one of the preceding claims which contains no more than 5% by weight of any fatty alcohol which is solid at 20°C.
16. A composition according to any one of the preceding  
10 claims which is a deodorant or antiperspirant composition comprising a deodorant or antiperspirant active.
17. A composition according to claim 11 which is an antiperspirant composition comprising a particulate  
15 antiperspirant active in suspension in said water-immiscible carrier liquid.
18. A composition according to any one of claims 4 to 10 which is an antiperspirant composition comprising an  
20 antiperspirant active dissolved in said disperse phase.
19. A composition according to any one of claim 16 to 18 wherein the antiperspirant active comprises an aluminium and/or zirconium halohydrate, an activated aluminium and/or

zirconium halohydrate, or an aluminium and/or zirconium complex or an activated aluminium and/or zirconium complex.

20. A composition according to claim 19 which is a  
5 halohydrate or complex in which aluminium and zirconium are both present.

21. A composition according to any one of claims 16 to 20  
wherein the proportion of antiperspirant active is from 5  
10 to 40% by weight of the composition.

22. A composition according to any one of the preceding claims in which a firm gel such that a penetrometer needle with a cone angle of 9 degrees 20 minutes, drops into the  
15 gel for no more than 30 mm when allowed to drop under a total weight of 50 grams for 5 seconds.

23. A composition according to any one of the preceding claims which is translucent or transparent.

20

24. A composition according to claim 23 which has at least 1%, and preferably at least 3%, light transmittance at 589 nm through a 1 cm thickness of the composition at 22°C.

**SUBSTITUTE SHEET (RULE 26)**

25. An antiperspirant product comprising a dispensing container having at least one aperture for delivery of the contents of the container, means for urging the contents of the container to the said aperture or apertures, and a  
5 composition according to any one of the preceding claims accommodated within the container.

26. A product according to claim 25 wherein the composition is in the form of a stick and the container has  
10 an open end at which an end portion of the stick of composition is exposed for use.

27. A process for the production of a composition according to any one of claims 1 to 20 comprising, not  
15 necessarily in any order, the steps of

- incorporating a structurant into a water-immiscible liquid carrier
- optionally mixing the liquid carrier with a disperse solid or liquid phase
- 20 • heating the liquid carrier or a mixture containing it to an elevated temperature at which the structurant is soluble in the water-immiscible liquid carrier.

followed by cooling or permitting the mixture to cool to a temperature at which it is thickened or solidified.

28. A process according to claim 27 which includes a step of pouring the mixture at elevated temperature into a dispensing container and allowing it to cool therein so as to produce a product according to claim 25 or claim 26.

29. A method for preventing or reducing perspiration on human skin comprising topically applying to the skin a composition according to any one of claims 16 to 20.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
19 October 2000 (19.10.2000)

PCT

(10) International Publication Number  
WO 00/61080 A3

- (51) International Patent Classification: A61K 7/32, 7/34, 7/38, 7/48  
Merseyside CH63 3JW (GB). HOPKINSON, Andrew: Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB).
- (21) International Application Number: PCT/GB00/01235
- (22) International Filing Date: 31 March 2000 (31.03.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 9908212.5 12 April 1999 (12.04.1999) GB
- (71) Applicant (for AE, AU, BB, CA, CY, DM, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, SD, SG, SL, SZ, TT, UG, ZA, ZW only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).
- (71) Applicant (for all designated States except AE, AU, BB, CA, CY, DM, GB, GD, GH, GM, IE, IL, IN, KE, LC, LK, LS, MN, MW, NZ, SD, SG, SL, SZ, TT, UG, ZA, ZW): UNILEVER NV [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).
- (71) Applicant (for IN only): HINDUSTAN LEVER LIMITED [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Mumbai 400 020 (IN).
- (72) Inventors: FRANKLIN, Kevin, Ronald; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral,
- (74) Agent: BAKER, Colin, J.; Eric Potter Clarkson, Park View House, 58 The Ropewalk, Nottingham NG1 5DD (GB).
- (81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW). Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM). European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:  
— With international search report.
- (88) Date of publication of the international search report: 3 May 2001
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 00/61080 A3

(54) Title: STRUCTURED COSMETIC COMPOSITIONS

(57) Abstract: A cosmetic composition contains a water-immiscible carrier liquid and a structurant therefor which is effective to gel the composition upon cooling from a temperature at which the structurant is a mobile solution in the carrier liquid. The carrier liquid may serve as a continuous phase in which a solid or liquid disperse phase is suspended. The structurant is a fully or partially esterified saccharide which contains no more than eight monosaccharide residues and has an enthalpy of gelation in the carrier liquid with a magnitude of at least 45 kJ/mole. This minimum enthalpy of gelation facilitates processing at conveniently accessible temperatures and promotes stability.

# INTERNATIONAL SEARCH REPORT

International Application No <b>PCT/GB 00/01235</b>		
<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7 A61K7/32 A61K7/34 A61K7/38 A61K7/48		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 7 A61K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ, CHEM ABS Data, EMBASE, MEDLINE, BIOSIS		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 635 165 A (PANITCH MAXIMO M) 3 June 1997 (1997-06-03)  abstract column 1, line 6 - line 22 column 3, line 55 - line 60 column 4, line 40 - column 5, line 38 column 6, line 6 - column 8, line 14 column 8, line 50 - line 61 column 9, line 40 - column 11, line 15 column 11, line 38 - line 55 column 13, line 38 - column 14, line 24 claims  --- -/--	1,3-7, 10-21, 27,29
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "A" document member of the same patent family		
Date of the actual completion of the international search 17 July 2000		Date of mailing of the international search report 26 01 2001
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel: (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Cielen, E

Form PCT/ISA/210 (second sheet) (July 1992)



# INTERNATIONAL SEARCH REPORT

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 849 276 A (MOTLEY CURTIS BOBBY ET AL) 15 December 1998 (1998-12-15)	1,3-6, 11-17, 19-21, 27,29
A	abstract  column 3, line 30 - line 46 column 5, line 22 - line 46 column 7, line 60 -column 10, line 32 column 12, line 48 -column 13, line 14 column 13, line 58 -column 14, line 14 column 14, line 47 - line 62 column 15, line 28 -column 16, line 10 column 17, line 40 -column 21, line 62 column 23, line 13 - line 24 ---	9,10
X	DATABASE WPI Week 198524 Derwent Publications Ltd., London, GB; AN 1985-143124 XP002142460 KOBAYASHI KOSE KK: "Stable oily gel compn. - comprises starch and sucrose fatty acid ester(s) and oily component." & JP 60 076543 A (KOBAYASHI KOSE KK), 1 May 1985 (1985-05-01) abstract ---	1,3-6,12
X	EP 0 736 545 A (CHIBA FLOUR MILLING ;KOSE CORP (JP)) 9 October 1996 (1996-10-09) abstract page 3, line 6 - line 43 page 5, line 38 - line 43 page 6, line 45 - line 57 example 3 claims ---	1,3,5,6, 12
A	WO 97 16163 A (PROCTER & GAMBLE) 9 May 1997 (1997-05-09)  abstract page 4, line 1 - line 15 page 4, line 35 -page 5, line 10 page 7, line 16 - line 27 page 9, line 13 - line 20 page 10, line 17 - line 31 page 11, line 27 -page 12, line 4 page 12, line 22 - line 24 page 14, line 18 -page 15, line 17 page 16, line 14 -page 17, line 1 claim 3  --- -/--	1,3,4, 10-14, 16-22, 27-29

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 00/01235

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	NOBOHIRO IDE, TAKESHI FUKUDA AND TAKEAKI MIYAMOTO: "GELATION OF FULLY ACYLATED CELLOBIOSE IN ALKANE SOLUTION" BULL. CHEM. SOC. JPN, vol. 68, 1995, pages 3423-3428, XP002127501 the whole document	
A	----- TAKADA A. ET AL.: "DISCOTIC COLUMNAR LIQUID CRYSTALS IN OLIGOSACCHARIDE DERIVATIVES III. ANOMERIC EFFECTS ON THE THERMO-MESOMORPHIC PROPERTIES OF CELLOBIOSE OCTA-ALKANOATES" LIQUID CRYSTALS, vol. 19, no. 4, 1995, pages 441-448, XP000545756 the whole document -----	

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/GB 00/01235

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:  
see FURTHER INFORMATION sheet, invention 1 (1.1, 1.2)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

## Continuation of Box I.2

(1) Present claims 1-24, 27-29 relate to a composition, a process for making such composition, and a method for applying such composition, and are defined by reference to the parameter "an enthalpy of gelation in the carrier liquid" with a specified value.

(2) Claims 1-24, 27-29 relate to a composition, a process and a method defined by reference to the parameter "an at least partially esterified saccharide which contains no more than eight monosaccharide residues".

(3) Claim 22 refers to a composition defined by reference to the parameter "a firm gel such that a penetrometer needle with a cone angle of 9 degrees 20 minutes, drops into the gel for no more than 30 mm when allowed to drop under a total weight of 50 grams for 5 seconds".

(4) Claim 24 refers to a composition defined by reference to the parameter "a light transmittance at 589 nm through a 1 cm thickness of the composition at 22 degrees centigrade of at least 1%, preferably at least 3%".

The use of these parameters in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is not fully possible to compare the parameters the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to the gellants alpha-cellobiose octa-octanoate (CB8, example 5, p.70), alpha-cellobiose octa-nonanoate (CB9 or esterified cellobiose C9, ex.5, p.71, ex. 6-8, 9.1-9.5, 10, 11, 13), alpha-cellobiose octa-decanoate (CB10 or esterified cellobiose C10, ex. 5, p.72, ex. 9.6-9.14), alpha-cellobiose octa-dodecanoate (CB12, ex.5, p.73), alpha-cellobiose octa-octadecanoate (CB18, ex. 5, p.74), esterified cellobiose C11 (ex.12), with due regard to the general idea underlying the application.

Claims searched partially: 1-24, 27-29

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-24, 27-29

1.1. Claims: 1-24,27,28

A cosmetic composition as claimed and the process for its preparation.

1.2. Claims: 1-24,29

A cosmetic composition as claimed and a method for preventing or reducing perspiration on human skin by topically applying such a composition.

2. Claims: 25,26

An antiperspirant product comprising a dispensing container.

Please note that all inventions mentioned under item 1, although not necessarily linked by a common inventive concept, could be searched without effort justifying an additional fee.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/01235

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5635165 A	03-06-1997	AU 725120 B AU 6971996 A BR 9610642 A CA 2232994 A CN 1202816 A EP 0852487 A HU 9901475 A JP 11514350 T PL 325960 A WO 9711678 A	05-10-2000 17-04-1997 18-05-1999 03-04-1997 23-12-1998 15-07-1998 30-08-1999 07-12-1999 17-08-1998 03-04-1997
US 5849276 A	15-12-1998	AU 5729698 A BR 9714061 A CN 1245414 A EP 0949895 A WO 9827939 A	17-07-1998 09-05-2000 23-02-2000 20-10-1999 02-07-1998
JP 60076543 A	01-05-1985	NONE	
EP 0736545 A	09-10-1996	JP 3019191 B JP 8277302 A CA 2173553 A US 5840883 A	13-03-2000 22-10-1996 06-10-1996 24-11-1998
WO 9716163 A	09-05-1997	BR 9611424 A EP 0858317 A US 5916546 A	23-02-1999 19-08-1998 29-06-1999

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> : <b>A61K 7/00</b>	<b>A2</b>	(11) International Publication Number: <b>WO 00/61080</b> (43) International Publication Date: <b>19 October 2000 (19.10.00)</b>
<p>(21) International Application Number: <b>PCT/GB00/01235</b></p> <p>(22) International Filing Date: <b>31 March 2000 (31.03.00)</b></p> <p>(30) Priority Data: <b>9908212.5</b> <b>12 April 1999 (12.04.99)</b> <b>GB</b></p> <p>(71) Applicant (for AE AU BB CA CY DM GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZA ZW only): <b>UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).</b></p> <p>(71) Applicant (for all designated States except AE AU BB CA CY DM GB GD GH GM IE IL IN KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZA ZW): <b>UNILEVER NV [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).</b></p> <p>(71) Applicant (for IN only): <b>HINDUSTAN LEVER LIMITED [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Mumbai 400 020 (IN).</b></p> <p>(72) Inventors: <b>FRANKLIN, Kevin, Ronald; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB). HOPKINSON, Andrew; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside CH63 3JW (GB).</b></p>	<p>(74) Agent: <b>BAKER, Colin, J.; Eric Potter Clarkson, Park View House, 58 The Ropewalk, Nottingham NG1 5DD (GB).</b></p> <p>(81) Designated States: <b>AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</b></p> <p><b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i></p>	
<p>(54) Title: <b>COSMETIC COMPOSITIONS</b></p> <p>(57) Abstract</p> <p>A cosmetic composition contains a water-immiscible carrier liquid and a structurant therefor which is effective to gel the composition upon cooling from a temperature at which the structurant is a mobile solution in the carrier liquid. The carrier liquid may serve as a continuous phase in which a solid or liquid disperse phase is suspended. The structurant is a fully or partially esterified saccharide which contains no more than eight monosaccharide residues and has an enthalpy of gelation in the carrier liquid with a magnitude of at least 45 kJ/mole. This minimum enthalpy of gelation facilitates processing at conveniently accessible temperatures and promotes stability.</p>		

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						



COSMETIC COMPOSITIONSFIELD OF THE INVENTION

5

The present invention relates to cosmetic compositions for application to human skin. Significant forms of the invention are concerned with antiperspirant compositions for application to human skin, especially  
10 the axilla. However, the invention can also be applied to other forms of cosmetic composition.

BACKGROUND OF THE INVENTION AND SUMMARY OF PRIOR ART

15

A wide variety of cosmetic compositions for application to human skin make use of a thickened or structured liquid carrier to deliver colour or some other active material to the surface of the skin. A significant example of such cosmetic compositions are  
20 antiperspirant compositions which are widely used in order to enable their users to avoid or minimise wet patches on their skin, especially in axillary regions.

Cosmetic compositions have been made in a variety of  
25 product forms. One of these is a so-called "stick" which is usually a bar of an apparently firm solid material

held within a dispensing container and which retains its structural integrity and shape whilst being applied. When a portion of the stick is drawn across the skin surface a film of the stick composition is transferred to the skin surface. Although the stick has the appearance of a solid article capable of retaining its own shape for a period of time, the material usually has a structured liquid phase so that a film of the composition is readily transferred from the stick to another surface upon contact. Examples of cosmetic compositions which are, or can be, marketed in a stick form are lipsticks, lip salves and eyebrow pencils. The stick form has been used in particular for deodorant and antiperspirant compositions where the composition includes a deodorant active material or an antiperspirant active material respectively.

Another possibility is that a stick is a softer solid composition accommodated in a dispensing container which in use extrudes the composition through one or more apertures.

Antiperspirant sticks and other cosmetic compositions can be divided into three categories. Suspension sticks contain a particulate material, notably a particulate antiperspirant active material, suspended

in a structured carrier liquid phase. Emulsion sticks normally have a hydrophilic phase forming an emulsion with a second, more hydrophobic, liquid phase. One of the phases contains an active material. Solution sticks  
5 typically have the active material dissolved in a structured liquid phase; this phase may be organic solvent or may be a mixture of water and a water-miscible organic solvent. This classification into suspension, emulsion and solution types can be applied to both firm  
10 and soft solid compositions.

Besides firm and soft sticks, a number of cosmetic compositions have taken the form of liquids which are formulated to be somewhat viscous and hence pour and flow  
15 more slowly than water. One example is antiperspirant compositions in liquid form, such as applied using a roll-on applicator.

There is substantial literature on the structuring  
20 or thickening of cosmetic compositions which is frequently accomplished using some form of thickening agent as part of the composition.

Some compositions have a substantial viscosity,  
25 which may even make them capable of retaining their own shape for a time, because of transient interactions

between molecules of a thickening agent in the liquid.

This is characteristic of compositions which are thickened with polymers. Thickening can be attributed to  
5 interactions between polymer molecules.

It is characteristic of such thickened compositions that their viscosity can be achieved or recovered on standing at room temperature. If subjected to shear  
10 their viscosity reduces (hence they are described as shear thinning) but the viscosity recovers towards its original value if the composition is subsequently allowed to stand at room temperature.

15 Compositions which have two phases, i.e. compositions which are an emulsion or a suspension may also have substantial viscosity, even to the extent of being able to sustain their own shape.

20 Here too it is characteristic of the composition that - provided the composition is stable - its viscosity will recover spontaneously if it is reduced by subjecting the composition to shear.

25 Compositions have also been given structure and an enhanced viscosity or rigidity by the incorporation of a

structurant (also referred to as a gellant or gelling agent) which causes the liquid to gel upon cooling from an elevated temperature.

5        Gel formation takes place as an exothermic event within a temperature range referred to as the gel point or gel temperature. Upon reheating, melting of the gel takes place as an endothermic event within a temperature range. When the gel melts, the structurant goes into  
10       solution in the liquid. Such gels can be disrupted by shearing and do not recover their viscosity for a long time, if at all unless remelted, although a small partial recovery may be observed.

15       One material which is well known to form gels is 12-hydroxystearic acid which is discussed in Terech et al "Organogels and Aerogels of Racemic and Chiral 12-hydroxy octadecanoic Acid", Langmuir Vol 10, 3406-3418, 1994. The material is commercially available from Ajinomoto and  
20       from Caschem.

US-A-5750096 and US-A-5489276 are two of several documents which teaches that gelation can be brought about using esters or amides of 12-hydroxystearic acid.

25

In these documents, especially the latter, there is

a proposal to enhance the efficacy of 12-hydroxystearic acid or other gellant by including a "nucleating agent". A range of possibilities for the nucleating agent are suggested, including esterified sucrose. The only  
5 function attributed to that material is to modify or promote the gelating action of another material.

Gelation with a waxy material, especially stearyl alcohol, has been mentioned in a great many documents.  
10 WO-A-98/43605 is a recent example.

N-acyl amino acid amides and esters are also known to structure liquids. We have established that they do so by forming fibrous networks. They are described in US  
15 patent 3969087. N-Lauroyl-L-glutamic acid di-n-butylamide is commercially available from Ajinomoto under their designation GP-1.

Further materials which have been disclosed as  
20 gelling agents are the amide derivatives of di and tribasic carboxylic acids set forth in WO 98/27954 notably alkyl N,N'dialkyl succinamides.

Yet another example of material which can be used to  
25 bring about gelation of a hydrophobic carrier liquid is lanosterol, as described in WO 97/11673 where it is used

in the preparation of soft, opaque gels as antiperspirant compositions WO 98/34588 also describes the use of lanosterol as a gellant for oil-based cosmetic compositions.

5

#### SUMMARY OF THE INVENTION

We have recognised that when a gel is formed, the solution of the structurant in a liquid may supercool  
10 before gelling commences, and in consequence the gel-melting temperature may be higher than the gel-formation temperature. If gel-formation takes place in a quiescent solution of the structurant the extent of supercooling may be substantial. We have observed that it varies from  
15 one structurant to another.

However, if the structurant is being used to prepare a product where a constituent such as a disperse phase is mixed into the hot liquid before gel formation, we have  
20 found that it is likely to be necessary to carry out this mixing operation at a temperature at which the structurant is fully soluble in the liquid. If an attempt is made to mix the composition at a temperature at which there is some supercooling, it is likely that the  
25 mixing will induce gelation to commence.

It is a consequence of this that when preparing structured liquid compositions containing a structurant to gel the liquid, all constituents of the composition must be subjected to a temperature high enough to  
5 dissolve the structuring agent.

We have now found that advantageous properties and processing can be provided by utilising as gelling agent an esterified saccharide which has an enthalpy of gelation  
10 of at least 45 kJoule per mole.

According to a first aspect of this invention there is provided a cosmetic composition comprising a water-immiscible carrier liquid and a structurant therefor  
15 which is effective to gel the composition upon cooling from a temperature at which the structurant is a mobile solution in the carrier liquid, characterised in that the structurant is a wholly or partially esterified saccharide which contains no more than eight  
20 monosaccharide residues and which has an enthalpy of gelation in the carrier liquid of at least 45 kJ/mole, preferably at least 48 kJ/mole or 50 kJ/mole.

The enthalpy of gelation can be determined by  
25 differential scanning calorimetry (DSC).



We have found that if the enthalpy of gelation is high (45 kJ per mole or more) compositions can be prepared with two advantages. One is that a composition can be prepared using moderate processing temperatures (which we have found to be important). The other is that the resulting gel is stable. By contrast, if the enthalpy of gelation is low, one or both of two disadvantages are observed. Rather high processing temperatures may be needed and/or a gel may be formed but then undergo unwanted progressive transformation during storage, such as crystals appearing and growing, softening of the composition or leakage of liquid from it.

Although the enthalpy of gelation is a property of the structurant and carrier liquid jointly, we have found that it is predominantly a property of the structurant. Consequently, the measurement of enthalpy of gelation in one or several representative liquids is valuable as technique (which can be carried out with a small sample and a standard instrument) to assess the suitability of a potential structurant. It may be desirable to take a measurement in any one of several representative liquids, since some structurants do not gel all hydrophobic carrier liquids. However, we have found that an 80:20 wt% mixture of decamethyl cyclopentasiloxane and

**SUBSTITUTE SHEET (RULE 26)**

isostearyl alcohol is generally suitable when assessing the suitability of a potential esterified saccharide structurant.

5           Therefore in a second aspect this invention provides a cosmetic composition comprising a water-immiscible carrier liquid and a structurant therefor which is effective to gel the composition upon cooling from a temperature at which the structurant is a mobile solution  
10 in the carrier liquid, characterised in that the structurant is a wholly or partially esterified saccharide which contains no more than eight monosaccharide residues and which structurant is able to gel an 80:20 wt% mixture of decamethyl cyclopentasiloxane  
15 and isostearyl alcohol with an enthalpy of gelation of at least 45 kJ/mole, preferably at least 48 or 50 kJ/mole.

          The esterified saccharide structurant will generally be such as to exist in the form of a network of fibres or  
20 strands within the water-immiscible carrier liquid.

          Preferably the structurant contains at least two but no more than five monosaccharide residues and is esterified at a majority of the esterified hydroxy  
25 groups.

Preferably the average number of carbon atoms in the esterifying acyl groups is at least 6, more preferably is from 6 to 8 up to 18 carbon atoms.

- 5        A composition of this invention may be a structured solution with active ingredient or colourant dissolved in the carrier liquid, or it may be a composition with a dispersed second phase, either a suspension with a solid active ingredient dispersed in the carrier liquid or an
- 10        emulsion with a second liquid phase dispersed in the carrier liquid. The second liquid phase may then be a solution of an antiperspirant active in a hydrophilic solvent.
- 15        A composition according to this invention may take the form of a firm gel with apparent rigidity, or a soft solid which is able to retain its own shape for a time (for example if it is taken out of a mould without being subjected to shear) but which is easily deformed by hand
- 20        pressure. Preferred within this invention are compositions which have sufficient rigidity that they can be regarded as firm solids. The hardness of such compositions can be measured with a penetrometer, in a manner which will be described in greater detail below.

25

Certain preferred forms of this invention are

concerned with compositions which are translucent or transparent. As is already known, translucent or transparent compositions can be obtained if it is possible to match the refractive indices of the different  
5 constituent phases present in the composition.

We have found that compositions within this invention which are a novel transparent or translucent emulsion can be obtained by formulating the composition  
10 to meet two criteria. Firstly the disperse phase and the continuous phase (consisting of the water-immiscible carrier liquid and the structurant contained within that liquid) should be formulated so that their refractive indices match. The refractive index of the continuous  
15 phase will be close to the refractive index of the water-immiscible carrier liquid in it. In order to achieve good light transmission through a composition, the refractive index of the water-immiscible continuous phase and the refractive index of the disperse phase should  
20 match within 0.003 units preferably 0.002 units.

Secondly, the matched refractive indices of these two phases should lie in a range which is an approximate match to the refractive index of the structurant. The  
25 closeness of match required will depend on the structurant which is used. The refractive index of a

structurant can be determined by making trial compositions as explained in more detail below. Such investigation will also show how closely the refractive index of the liquid must be matched to the structurant.

5

A composition of this invention will generally be marketed in a container by means of which it can be applied at time of use. This container may be of conventional type.

10

Another aspect of the invention therefore provides a cosmetic composition comprising a dispensing container having at least one aperture for delivery of the contents of the container, means for urging the contents of the container to the said aperture or apertures, and a composition of either of the previous aspects of the invention in the container. Preferred is that a composition of this invention is sufficiently rigid to be accommodated as a stick product in a dispensing container having an open end at which an end portion of the stick of composition is exposed for use.

The compositions of this invention can be produced by processes in which the composition is produced as a mobile liquid at an elevated temperature and allowed to cool to permit gel-formation.

Thus, according to a further aspect of the present invention there is provided a process for the production of an antiperspirant composition comprising, not necessarily in any order, the steps of

- 5 • incorporating an esterified saccharide structurant into a water-immiscible liquid carrier
  - optionally mixing the liquid carrier with a disperse solid or liquid phase,
  - heating the liquid carrier or a mixture containing it
  - 10 to an elevated temperature at which the structurant is soluble in the water-immiscible liquid carrier,
- suitably followed by
- introducing the mixture into a mould which
  - 15 preferably is a dispensing container, and then
  - cooling or permitting the mixture to cool to a temperature at which it is thickened or solidified.

In this invention it is possible and indeed

20 preferred that the step of mixing with a disperse phase, and any subsequent steps, are carried out at a temperature not exceeding 90°C and possibly not exceeding 85°C.

It may be possible to keep below these temperatures

25 throughout the process.

According to a yet further aspect of the present invention, there is provided a method for preventing or reducing perspiration on human skin comprising topically applying to the skin a composition as set forth earlier comprising an antiperspirant active, a water-immiscible liquid carrier and an esterified saccharide structurant therefor.

#### DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS

10

Measurement of enthalpy of gelation can be carried out using a small sample and standard DSC techniques.

Measurement should be carried out at a slow cooling rate and to promote consistency in measurement, it should, if possible, be carried out with the concentration in a standardised range or approximating to a standard value.

20 We have preferred to carry out measurement at a concentration of structurant in the liquid which is not over 8% by weight, preferably from 3%, better 6%, up to 8% by weight. Results at such concentrations are generally a close approximation to results at a  
25 standardised concentration of 7.5% by weight.

For any structurant which cannot dissolve at such a concentration, an alternative standardised concentration would be 3% by weight.

5       A gel may first be made by heating and cooling, and a sample of gel sealed in a calorimeter capsule. Alternatively the appropriate weights of liquid and structurant could be sealed in a calorimeter capsule, heated and allowed to cool to a gel in the capsule.

10

In a preferred procedure a gel is prepared containing from 7 to 7.5% by weight of structuring agent.

Approximately 20mg of the gel (for example between 18 and 22 mg) is weighed into a calorimeter capsule and sealed.

15       It is then heated at 10K/minute to a temperature at which the structuring agent is known to be fully soluble in the liquid, held for one minute at this temperature and then a DSC scan is taken while cooling at 2K/minute.

20       The scan is repeated with a capsule containing approximately 20mg of decamethyl cyclopentadisiloxane and in accordance with normal DSC technique, data collected with the liquid alone (multiplied by a scaling factor if necessary) is subtracted from the data collected with the  
25       gel, so that the gel-formation exotherm appears as a departure from a flat baseline. The enthalpy is the area



between the peak and the baseline.

We have found it appropriate to carry out measurements, both on the gel and on the liquid alone,  
5 over a broad range of temperatures, such as from -50°C to +150°C for the sake of accuracy in subtracting one measurement from the other.

For calculation it is assumed that the exotherm  
10 (heat given out during gel formation) comes from the whole quantity of structuring agent present.

#### Structurant

15 A number of organic compounds are known to possess the ability to gel hydrophobic organic liquids such as water-immiscible hydrocarbon and/or silicone oils by formation of a network of fibres or strands which extends throughout the liquid, thereby gelling the liquid. Such  
20 materials are generally non-polymeric, being monomers or dimers with molecular weight below 10,000 rather than polymers with more than 8 repeat units or with molecular weight above 10,000.

Materials with this property have been reviewed by  
25 Terech and Weiss in "Low Molecular Mass Gelators of

Organic Liquids and the Properties of their Gels" Chem.  
Rev 97, 3133-3159 [1997] and by Terech in Chapter 8,  
"Low-molecular weight Organogelators" of the book  
"Specialist surfactants" edited by I D Robb, Blackie  
5 Academic Professional, 1997.

It is characteristic of such structurants that

- they are able to gel the organic liquid in the  
absence of any disperse phase
- 10 • the structured liquids are obtainable by cooling  
from an elevated temperature at which the  
structurant is in solution in the liquid - this  
solution being mobile and pourable
- the structured liquid becomes more mobile if  
15 subjected to shear or stress
- the structure does not spontaneously recover within  
24 hours if the sheared liquid is left to stand at  
room temperature even though a small partial  
recovery may be observed
- 20 • the structure can be recovered by reheating to a  
temperature at which the structurant is in solution  
in the liquid, and allowing it to cool back to room  
temperature.

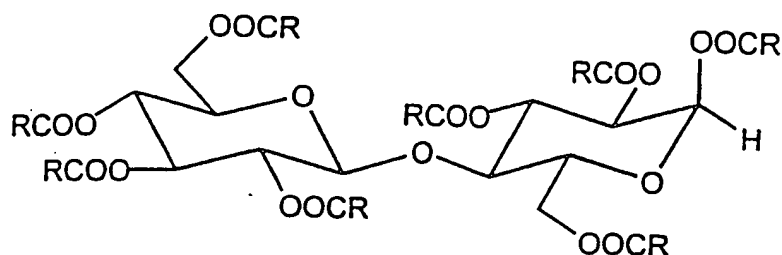
25 It appears that such structurants operate by  
interactions which are permanent unless disrupted by

shear or heating. Such structurants operate by forming a network of strands or fibres extending throughout the gelled liquid. In some cases these fibres can be observed by electron microscopy, although in other cases the  
5 observation of the fibres which are believed to be present is prevented by practical difficulties in preparing a suitable specimen. When observed, the fibres in a gel are generally thin (diameter less than  $0.5\mu$ , often less than  $0.2\mu$ ) and appear to have numerous  
10 branches or interconnections.

From our observations made using differential scanning calorimetry we believe that fibrous networks consist of crystalline material. The crystalline fibres  
15 may or may not be the same polymorph as macroscopic crystals obtained by conventional crystallization from a solvent.

A novel structurant which is the subject of a co-  
20 pending application and which may be used in this invention is an ester of cellobiose and a fatty acid, preferably of 6 to 13 carbon atoms especially 8 to 11 carbon atoms. Preferably the cellobiose is fully esterified, or nearly so, and is in the  
25  $\alpha$ -anomeric form.

The structure of such a compound in its  $\alpha$ -anomeric form is:



- 5 where R is an alkyl or alkenyl chain of 5 to 12 carbon atoms so that the acyl group contains 6 to 13 carbon atoms. Particularly preferred acyl groups incorporate a linear alkyl chain of 7 to 9 or 10 carbon atoms and are thus octanoyl, nonanoyl, decanoyl or undecanoyl.

10

- The acyl groups may have a mixture of chain lengths but it is preferred that they are similar in size and structure. Thus it is preferred that all of the acyl groups are aliphatic and at least 90% of the acyl groups have a chain length within a range such that the shorter and longer chain lengths in the range differ by no more than two carbon atoms, i.e. length in a range from  $m - 1$  to  $m + 1$  carbon atoms where the mean acyl chain length  $m$  has a value in a range from 7 to 10 or 11. Commercially available feedstocks for these acyl groups are likely to include a small percentage of acyl groups which differ

from the majority and may have a branched rather than linear chain. Thus it is likely that more than 90% but less than 100% of the acyl groups will meet the desired criterion of chain lengths in a range from  $m - 1$  to  $m + 1$  carbon atoms.

Linear aliphatic acyl groups may be obtained from natural sources, in which case the number of carbon atoms in the acyl group is likely to be an even number or may be derived synthetically from petroleum as the raw material in which case both odd and even numbered chain lengths are available.

Synthetic methods for the esterification of saccharides are well known. The esterification of cellobiose has been reported by Takada et al in *Liquid Crystals*, (1995) Volume 19, pages 441-448. This article gives a procedure for the production of the alpha anomers of cellobiose octa-alkanoates by esterification of  $\beta$ -cellobiose using an alkanoic acid together with trifluoroacetic anhydride.

For this invention the structurant is a material from this category discussed above but selected so that it also satisfies the criterion of an enthalpy of gelation exceeding 45 kJoule per mole.

Carrier liquid

The water-immiscible carrier liquid in the continuous phase comprises one or a mixture of materials which are relatively hydrophobic so as to be immiscible in water. Some hydrophilic liquid may be included in the carrier, provided the overall carrier liquid mixture is immiscible with water. It will generally be desired that this carrier is liquid (in the absence of structurant) at temperatures of 15°C and above. It may have some volatility but its vapour pressure will generally be less than 4 kPa (30mmHg) at 25°C so that the material can be referred to as an oil or mixture of oils. More specifically, it is desirable that at least 80% by weight of the hydrophobic carrier liquid should consist of materials with a vapour pressure not over this value of 4 kPa at 25°C.

It is preferred that the hydrophobic carrier material includes a volatile liquid silicone, i.e. liquid polyorganosiloxane. To class as "volatile" such material should have a measurable vapour pressure at 20 or 25°C. Typically the vapour pressure of a volatile silicone lies in a range from 1 or 10 Pa up to 2 kPa at 25°C.

It is desirable to include volatile silicone because

it gives a "drier" feel to the applied film after the composition is applied to skin.

Volatile polyorganosiloxanes can be linear or cyclic  
5 or mixtures thereof. Preferred cyclic siloxanes include polydimethylsiloxanes and particularly those containing from 3 to 9 silicon atoms and preferably not more than 7 silicon atoms and most preferably from 4 to 6 silicon atoms, otherwise often referred to as cyclomethicones.  
10 Preferred linear siloxanes include polydimethylsiloxanes containing from 3 to 9 silicon atoms. The volatile siloxanes normally by themselves exhibit viscosities of below  $10^{-5}$  m<sup>2</sup>/sec (10 centistokes), and particularly above  $10^{-7}$  m<sup>2</sup>/sec (0.1 centistokes), the linear siloxanes  
15 normally exhibiting a viscosity of below  $5 \times 10^{-6}$  m<sup>2</sup>/sec (5 centistokes). The volatile silicones can also comprise branched linear or cyclic siloxanes such as the aforementioned linear or cyclic siloxanes substituted by one or more pendant -O-Si(CH<sub>3</sub>)<sub>3</sub> groups. Examples of  
20 commercially available silicone oils include oils having grade designations 344, 345, 244, 245 and 246 from Dow Corning Corporation; Silicone 7207 and Silicone 7158 from Union Carbide Corporation; and SF1202 from General Electric.

25

The hydrophobic carrier employed in compositions

SUBSTITUTE SHEET (RULE 26)

herein can alternatively or additionally comprise non-volatile silicone oils, which include polyalkyl siloxanes, polyalkylaryl siloxanes and polyethersiloxane copolymers. These can suitably be selected from dimethicone and  
5 dimethicone copolyols. Commercially available non-volatile silicone oils include Dow Corning 556 and Dow Corning 200 series.

The water-immiscible liquid carrier may contain from  
10 0 to 100% by weight of one or more liquid silicones. Preferably, there is sufficient liquid silicone to provide at least 10%, better at least 15%, by weight of the whole composition. If silicone oil is used, volatile silicone preferably lies in a range from 20% possibly from 30 or  
15 40% up to 100% of the weight of the water-immiscible carrier liquid. In many instances, when a non-volatile silicone oil is present, its weight ratio to volatile silicone oil is chosen in the range of from 1:3 to 1:40.

20 Silicon-free hydrophobic liquids can be used instead of, or more preferably in addition to liquid silicones. Silicon-free hydrophobic organic liquids which can be incorporated include liquid aliphatic hydrocarbons such as mineral oils or hydrogenated polyisobutene, often selected  
25 to exhibit a low viscosity. Further examples of liquid hydrocarbons are polydecene and paraffins and isoparaffins



of at least 10 carbon atoms.

Other hydrophobic carriers are liquid aliphatic or aromatic esters.

5

Suitable aliphatic esters contain at least one long chain alkyl group, such as esters derived from C<sub>1</sub> to C<sub>20</sub> alkanols esterified with a C<sub>8</sub> to C<sub>22</sub> alkanolic acid or C<sub>6</sub> to C<sub>10</sub> alkanedioic acid. The alkanol and acid moieties or mixtures thereof are preferably selected such that they each have a melting point of below 20°C. These esters include isopropyl myristate, lauryl myristate, isopropyl palmitate, diisopropyl sebacate and diisopropyl adipate.

15

Suitable liquid aromatic esters, preferably having a melting point of below 20°C, include fatty alkyl benzoates. Examples of such esters include suitable C<sub>8</sub> to C<sub>18</sub> alkyl benzoates or mixtures thereof.

20

Further instances of suitable hydrophobic carriers comprise liquid aliphatic ethers derived from at least one fatty alcohol, such as myristyl ether derivatives e.g. PPG-3 myristyl ether or lower alkyl ethers of polyglycols such as PPG-14 butyl ether.

25

Aliphatic alcohols which are solid at 20°C, such as stearyl alcohol are preferably absent or present in low concentration such as less than 5% by weight of the whole composition since these lead to visible white deposits  
5 when a composition is used.

However, aliphatic alcohols which are liquid at 20°C may be employed. These include branched chain alcohols of at least 10 carbon atoms such as isostearyl alcohol and  
10 octyl dodecanol.

Very polar materials are preferably excluded or present in only small quantity in the water-immiscible carrier liquid. Preferably therefore, this liquid or  
15 mixture of liquids contains not more than 10% of its own weight, better not more than 5%, of any constituent which is a water-miscible compound.

Silicon-free liquids can constitute from 0-100% of  
20 the water-immiscible liquid carrier, but it is preferred that silicone oil is present and that the amount of silicon-free constituents preferably constitutes up to 50 or 60% and in many instances from 10 or 15% up to 50 or 60% by weight of the carrier liquid.

25

If any oxygen-containing silicon-free organic

**SUBSTITUTE SHEET (RULE 26)**

liquids are included in the hydrophobic carrier liquid, the amount of them is likely to be not over 70% by weight of the carrier liquid. Smaller amounts, ranging up to 20, 30 or 35% by weight are likely.

5

The carrier liquid must be compatible with the structurant. If the structurant is too soluble or conversely is very insoluble in the carrier liquid it may fail to form a gel and the carrier liquid should be  
10 modified to alter its polarity.

Liquid Disperse Phase

If the composition is an emulsion in which the esterified saccharide acts as a structurant in the continuous phase, the emulsion will contain a more polar disperse phase. The disperse phase may be a solution of an active ingredient.

The hydrophilic disperse phase in an emulsion normally comprises water as solvent and can comprise one or more water soluble or water miscible liquids in addition to or replacement for water. The proportion of water in an emulsion according to the present invention is often selected in the range of up to 60%, and particularly from 10% up to 40% or 50% of the whole formulation.

One class of water soluble or water-miscible liquids comprises short chain monohydric alcohols, e.g. C<sub>1</sub> to C<sub>4</sub>, and especially ethanol or isopropanol, which can impart a deodorising capability to the formulation. A further class of hydrophilic liquids comprises diols or polyols preferably having a melting point of below 40°C, or which are water miscible. Examples of water-soluble or water-miscible liquids with at least one free hydroxy group include ethylene glycol, 1,2-propylene glycol, 1,3-

butylene glycol, hexylene glycol, diethylene glycol,  
dipropylene glycol, 2-ethoxyethanol, diethylene glycol  
monomethylether, triethyleneglycol monomethylether and  
sorbitol. Especially preferred are propylene glycol and  
5 glycerol.

In an emulsion the disperse phase is likely to  
constitute from 5 to 80 or 85% of the weight of the  
composition preferably from 5 to 50 or 65% more  
10 preferably from 25 or 35% up to 50 or 65%, while the  
continuous phase with the structurant therein provides  
the balance from 15 or 35% up to 95% of the weight of the  
composition. Compositions with a high proportion of  
disperse phase i.e. from 65 to 85% disperse phase may be  
15 advantageous because the large proportion of disperse  
phase can make a contribution to hardness.

An emulsion composition will generally include one or  
more emulsifying surfactants which may be anionic,  
20 cationic, zwitterionic and/or nonionic surfactants. The  
proportion of emulsifier in the composition is often  
selected in the range up to 10% by weight and in many  
instances from 0.1 or 0.25 up to 5% by weight of the  
composition. Most preferred is an amount from 0.1 or  
25 0.25 up to 3% by weight. Nonionic emulsifiers are  
frequently classified by HLB value. It is desirable to

use an emulsifier or a mixture of emulsifiers with an overall HLB value in a range from 2 to 10 preferably from 3 to 8.

5        It may be convenient to use a combination of two or more emulsifiers which have different HLB values above and below the desired value. By employing the two emulsifiers together in appropriate ratio, it is readily feasible to attain a weighted average HLB value that  
10 promotes the formation of an emulsion.

Many suitable emulsifiers of high HLB are nonionic ester or ether emulsifiers comprising a polyoxyalkylene moiety, especially a polyoxyethylene moiety, often  
15 containing from about 2 to 80, and especially 5 to 60 oxyethylene units, and/or contain a polyhydroxy compound such as glycerol or sorbitol or other alditol as hydrophilic moiety. The hydrophilic moiety can contain polyoxypropylene. The emulsifiers additionally contain a  
20 hydrophobic alkyl, alkenyl or aralkyl moiety, normally containing from about 8 to 50 carbons and particularly from 10 to 30 carbons. The hydrophobic moiety can be either linear or branched and is often saturated, though it can be unsaturated, and is optionally fluorinated.  
25 The hydrophobic moiety can comprise a mixture of chain lengths, for example those deriving from tallow, lard,